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Contents

editorial

Dmitri Mendeleev and his Periodic Table of Elements

Every few years, with more and more advances in nuclear physics, Dmitri's horoscope of elements is proved right again and again.

Every laboratory having powerful accelerations is in the game of the discovery of new elements which are fitted into the table of elements with their properties proving the predictions of the Grand Master.

Heavier the element, greater should be the power of the accelerators and more difficult to separate the isotopes. Apart from making the discovery, the scientists have also something to teach us—Cooperation is for success and confrontation ends in failure.

GSI laboratory in Germany, Gutenberg university from Mainz and Helmholtz university, also from Mainz with a team of 72 scientists from 16 institutions in Australia, Finland, Germany, India, Japan, Norway, Sweden, Switzerland, the UK and the USA had cooperated in this work.

The difficulties—heavier the element, greater is the difficulty to produce the element, and shorter the life-time, more hurdles to be crossed.

A special target of berkelium metal was used. But of the huge number of reaction products, atoms of elements 117 were separated by the study of radioactive decay. This was further confirmed by the study of the decay elements.

Yes—Atomic and Nuclear researches are very exciting. Education and Research in every field have no barriers. They are the backbone of developed countries. This is also a call to our non students to look for the exciting areas in research.

Anil Ahlawat
Editor

CHEMISTRY MUSING

Chemistry Musing was started from August '13 issue of Chemistry Today with the suggestion of Shri Mahabir Singh. The aim of Chemistry Musing is to augment the chances of bright students preparing for JEE (Main and Advanced) / AIPMT / AIIMS / Other PMTs & PETs with additional study material.

In every issue of Chemistry Today, 10 challenging problems are proposed in various topics of JEE (Main and Advanced) / AIPMT. The detailed solutions of these problems will be published in next issue of Chemistry Today.

The readers who have solved five or more problems may send their solutions. The names of those who send atleast five correct solutions will be published in the next issue.

We hope that our readers will enrich their problem solving skills through "Chemistry Musing" and stand in better stead while facing the competitive exams.

PROBLEM Set 11

JEE MAIN/PMTS

1. An ideal gas has a specific heat at constant pressure, $C_p = \frac{5}{2}R$. The gas is kept in a closed vessel of volume 0.0083 m^3, at a temperature 300 K and pressure 1.6×10^6 N/m^2. An amount of 2.49×10^4 J of energy is supplied to the gas. The final temperature and pressure of the gas respectively are [Given : $R = 8.3$ J K^{-1} mol^{-1}]

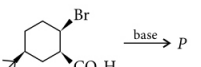
(a) 675 K, 4.0×10^6 N/m^2
(b) 375 K, 3.59×10^6 N/m^2
(c) 375 K, 1.6×10^6 N/m^2
(d) 675 K, 3.59×10^6 N/m^2

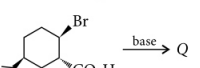
2. Which of the following statements about *p*-block elements are incorrect?

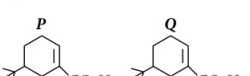
(I) Salts of hypohalous acids are alkaline in nature due to hydrolysis.
(II) BiF_3 is covalent while NF_3 and PF_3 are ionic in nature.
(III) Boiling point of water is higher than that of hydrogen fluoride.
(IV) Stability of hydrides of carbon family increases down the group from C to Pb.

(a) II and IV (b) I and III
(c) III and IV (d) All of these.

3. Identify the products of the following reactions :





(a) 

(b) 

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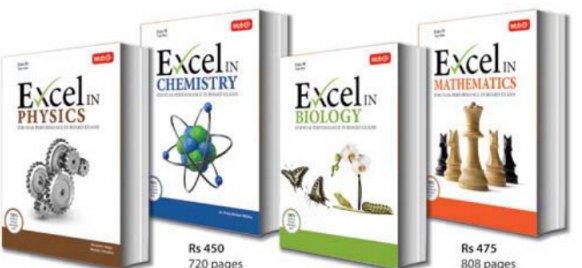

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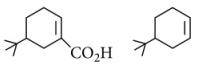
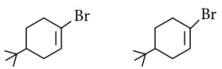
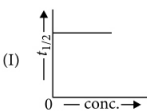
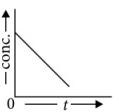
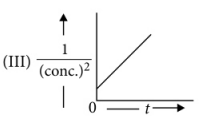
(c) 

(d) 

4. Kinetics of three reactions are graphically shown as :

(I) 

(II) 

(III) 

The order of the reactions are

(a) I and II are 1 and 2 respectively
(b) II and III are zero and 1 respectively
(c) I and III are 1 and 3 respectively
(d) III and I are 3 and zero respectively.

5. Which of the following is not the correct order of solubility of given compounds in water?

(a) CsF > CsCl > CsBr > CsI
(b) $NaCl > BaCl_2 > AlCl_3$
(c) $LiNO_3 < NaNO_3 < KNO_3 < CsNO_3$
(d) $NaCl > Na_2SO_4 > Na_3PO_4$

JEE ADVANCED

6. An ideal solution is formed by mixing two volatile liquids *A* and *B*. x_A and x_B are the mole fractions of *A* and *B* respectively in the solution and y_A and y_B are the mole fractions of *A* and *B* respectively in the vapour phase. A plot of $1/y_A$ along *y*-axis against $1/x_A$ along *x*-axis gives a straight line. The slope of the straight line is

(a) p_B°/p_A° (b) p_A°/p_B°
(c) $p_B^\circ - p_A^\circ$ (d) $p_A^\circ - p_B^\circ$

(where, p_A° and p_B° are the vapour pressures of the pure components *A* and *B* respectively.)

COMPREHENSION

Nucleophilic substitution reactions are mainly of two types S_N1 and S_N2.

S_N1 reaction proceeds through the formation of carbocation in polar protic solvents. Solvent itself acts as nucleophile in this reaction. Racemization takes place in S_N1 reaction.

S_N2 reaction proceeds with strong nucleophiles in polar aprotic solvents. 3° halides do not give S_N2 reaction. Inverted products are obtained in this reaction and mechanism of reaction occurs through the formation of transition state.

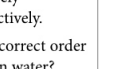
7. Which of the following compounds will give S_N1 reaction?

(a)

(b) CH_3Cl
(c) CH_3CH_2Br
(d) $IC_6H_4OCH_3$

8. Which one of the following will give racemised product in C_2H_5OH?

(a)  (b) 

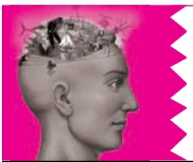
(c)  (d) 

INTEGER VALUE

9. The rate of emission of quanta per second (in 10^{19} s^{-1}) when a 25 watt bulb emits monochromatic yellow light of wavelength 0.57 μm, is

10. Among the following the total number of outer octahedral complexes is

$[Co(ox)_3]^{3-}$, $[Fe(H_2O)_6]^{3+}$, $[Ni(NH_3)_6]^{2+}$, $[Mn(CN)_6]^{4-}$, $[Cr(H_2O)_6]^{3+}$, $[CoF_6]^{3-}$, $[Fe(CN)_6]^{3-}$



EXAMINER'S MIND NCERT CLASS XI

The questions given in this column have been prepared strictly on the basis of NCERT Chemistry for Class XI. This year JEE (Main & Advanced) /AIPMT / AIIMS/other PMTs have drawn their papers heavily from NCERT books.

SOME BASIC CONCEPTS OF CHEMISTRY | STRUCTURE OF ATOM

SECTION - I

Only One Option Correct Type

This section contains 20 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

1. The largest number of atoms are present in
(a) 5 g of NH_3 (b) 11 g of CO_2
(c) 8 g of SO_2 (d) 4 g of H_2

2. Chlorine exists in two isotopic forms, Cl-37 and Cl-35 but its atomic mass is 35.5. This indicates the ratio of Cl-37 and Cl-35 is approximately
(a) 1 : 2 (b) 1 : 1
(c) 1 : 3 (d) 3 : 1

3. Mark the rule which is not correctly stated about the determination of significant figures.
(a) Zeros preceding to first non-zero digit are not significant.
(b) Zeros between two non-zero digits are not significant.
(c) Zeros at the end or right of the number are significant if they are on the right side of decimal point.
(d) All non-zero digits are significant.

4. An electron in a hydrogen atom in its ground state absorbs 1.50 times as much energy as the minimum energy required for it to escape from the atom. The wavelength of the emitted electron is
(a) 13.6×10^{-8} m (b) 1.8×10^{-18} m
(c) 1.55×10^{6} m (d) 4.7×10^{-10} m

5. Haemoglobin contains 0.334% of iron by weight. The molecular weight of haemoglobin is approximately 67200. The number of iron atoms (Atomic weight of Fe is 56) present in one molecule of haemoglobin is
(a) 4 (b) 6
(c) 3 (d) 2

6. An ion with mass number 56 contains 3 units of positive charge and 30.4% more neutrons than electrons. The ion is
(a) $^{56}_{28}Ni^{3+}$ (b) $^{56}_{26}Fe^{3+}$
(c) $^{56}_{27}Co^{3+}$ (d) $^{56}_{24}Cr^{3+}$

7. If one gram of a metal carbonate gave 0.56 g of its oxide on heating, then equivalent weight of the metal will be
(a) 30 (b) 40
(c) 25 (d) 20

8. If the uncertainty in the position of an electron is zero, the uncertainty in its momentum would be
(a) zero (b) greater than $h/4\pi$
(c) less than $h/4\pi$ (d) infinite.

9. Which of the following statements indicates that law of multiple proportion is being followed?
(a) Sample of carbon dioxide taken from any source will always have carbon and oxygen in the ratio 1:2.
(b) Carbon forms two oxides namely CO_2 and CO, where masses of oxygen which combine with fixed mass of carbon are in the simple ratio 2:1.

(c) When magnesium burns in oxygen, the amount of magnesium taken for the reaction is equal to the amount of magnesium in magnesium oxide formed.
(d) At constant temperature and pressure, 200 mL of hydrogen will combine with 100 mL of oxygen to produce 200 mL of water vapour.

10. How many electrons in an atom with atomic number 105 can have $(n + l) = 8$?
(a) 30 (b) 17
(c) 15 (d) unpredictable

11. The ratio of amounts of H_2S needed to precipitate all the metal ions from 100 mL of 1 M $AgNO_3$ and 100 mL of 1 M $CuSO_4$ will be
(a) 1 : 1 (b) 1 : 2
(c) 2 : 1 (d) None of these.

12. Chloride ion and potassium ion are isoelectronic. Then
(a) potassium ion is relatively bigger
(b) depends on the other cation and anion
(c) their sizes are same
(d) chloride ion is bigger than potassium ion.

13. A compound of iron and chlorine is soluble in water. An excess of silver nitrate was added to precipitate the chloride ion as silver chloride. If a 134.8 mg of the compound gave 304.8 mg of AgCl, what is the formula of the compound?
(a) $FeCl_6$ (b) $FeCl_3$
(c) $FeCl_2$ (d) $FeCl_4$

14. Which of the following sets of quantum numbers violates the rules of quantum mechanics?
(a) $n = 3, l = 2, m_l = -3, m_s = +1/2$
(b) $n = 3, l = 1, m_l = -1, m_s = -1/2$
(c) $n = 4, l = 0, m_l = 0, m_s = +1/2$
(d) $n = 3, l = 2, m_l = -2, m_s = +1/2$

15. The total number of electrons present in 18 mL of water (density of water is 1 g mL^{-1}) is
(a) 6.02×10^{23} (b) 6.02×10^{22}
(c) 6.02×10^{24} (d) 6.02×10^{25}

16. A 3*p*-orbital has
(a) two non-spherical nodes
(b) two spherical nodes
(c) one spherical and one non-spherical node
(d) one spherical and two non-spherical nodes.

17. In a reaction container, 100 g of hydrogen and 100 g of Cl_2 are mixed for the formation of HCl gas. What is the limiting reagent and how much HCl is formed in the reaction?
(a) H_2 is limiting reagent and 36.5 g of HCl are formed.
(b) Cl_2 is limiting reagent and 102.8 g of HCl are formed.
(c) H_2 is limiting reagent and 142 g of HCl are formed.
(d) Cl_2 is limiting reagent and 73 g of HCl are formed.

18. In a photoelectric experiment, doubling the intensity of the incident light results in emitting electrons
(a) in a larger number
(b) in a lesser number
(c) associated with higher frequency
(d) associated with lower frequency.

19. What will be the molarity (in mol L^{-1}) of a solution, which contains 5.85 g of $NaCl_{(s)}$ per 500 mL?
(a) 4 (b) 20
(c) 0.2 (d) 2

20. Time taken for an electron to complete one revolution in Bohr orbit of hydrogen atom is
(a) $\frac{4\pi^2 mr^2}{nh}$ (b) $\frac{nh}{4\pi^2 mr}$
(c) $\frac{2\pi mr}{n^2h^2}$ (d) $\frac{h}{2\pi mr}$

SECTION - II

One or More Options Correct Type

This section contains 5 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONE or MORE are correct.

21. Which of the following statements about $_{15}P^{32}$ and $_{16}S^{32}$ are correct?
(a) If a neutron is added to the nucleus of $_{15}P^{32}$, $_{16}S^{32}$ is produced.

(b) Total number of nucleons in these two are same.
(c) Both contain 32 electrons.
(d) The phosphorus atom has more neutrons than the sulphur atom.

22. The atomic weights of two elements *A* and *B* are 20 and 40 respectively. Which of the following statements are correct for these two elements?
(a) *x* g of *A* contains *y* atoms which is equal to atoms present in *x* g of *B*.
(b) *x* g of *A* contains *y* atoms which is equal to atoms present in 2*x* g of *B*.
(c) At STP, *x* L of monoatomic gas *A* is equal to *x* L of monoatomic gas *B*.
(d) At STP, *x* L of monoatomic gas *A* weighs *y* g and *y* g monoatomic gas *B* is measured *xz*.

23. Light of wavelength λ shines on a metal surface with intensity *x* and the metal emits *y* electrons per second of average energy, *z*. What will happen to *y* and *z* if *x* is doubled?
(a) *y* will be doubled and *z* will become half.
(b) *y* will remain same and *z* will be doubled.
(c) Both *y* and *z* will be doubled.
(d) *y* will be doubled but *z* will remain same.

24. 1.0 g of Mg is burnt in a closed vessel which contains 0.5 g of O_2. It means
(a) equivalent of MgO is equal to that of magnesium (1/12)
(b) equivalent of MgO is equal to that of oxygen (0.5 g/8)
(c) equivalent of oxygen = equivalent of magnesium = equivalent of MgO in the reaction
(d) moles of oxygen = moles of magnesium = moles of MgO in the reaction.

25. In the second group of solutions, the values of ψ and ψ^2 depend upon
(a) the distance from the nucleus
(b) any one of the direction in space
(c) any two of the directions in space
(d) all the directions in space.

SECTION - III

Paragraph Type

This section contains 2 paragraphs each describing theory, experiment, data, etc. Six questions relate to two paragraphs with three questions on each paragraph. Each question of a paragraph has only one correct answer among the four choices (a), (b), (c) and (d).

Paragraph for Questions 26 to 28

An empirical formula represents the simplest whole number ratio of various atoms present in a compound whereas the molecular formula shows the exact number of different types of atoms present in a molecule of a compound.
If the mass per cent of various elements present in a compound is known, its empirical formula can be determined. Molecular formula can further be obtained if the molar mass is known.

26. 0.30 g of an organic compound containing C, H and O on combustion gave 0.44 g CO_2 and 0.18 g H_2O. If 1 mole of compound weighs 60, then molecular formula of the compound is
(a) $C_2H_4O_2$ (b) CH_2O
(c) C_3H_8O (d) C_4H_{12}

27. The empirical formula of an acid is CH_2O_2, the probable molecular formula of acid may be
(a) CH_2O (b) CH_2O_2
(c) $C_2H_4O_2$ (d) $C_3H_6O_4$

28. In a compound C, H and N are present in 9 : 1 : 3.5 by weight. If molecular weight of the compound is 108, then the molecular formula of the compound is
(a) $C_2H_6N_2$ (b) C_3H_4N
(c) $C_6H_8N_2$ (d) $C_9H_{12}N_3$

Paragraph for Questions 29 to 31

The hydrogen spectrum consists of several series of lines named after their discoverers.
All series of lines in the hydrogen spectrum could be described by the following expression:

$$\bar{\nu} = 109{,}677\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{cm}^{-1}$$

where $n_1 = 1, 2.....$
$n_2 = n_1 + 1, n_1 + 2.....$
The value 109,677 cm^{-1} is called the Rydberg constant for hydrogen.

29. When the electrons of hydrogen atom return to L shell from shells of higher energy, we get a series of lines in the spectrum. This series is called

(a) Brackett series (b) Paschen series
(c) Balmer series (d) Lyman series.

30. Given below are the spectral lines for an atom of hydrogen. Mark the lines which are not correctly matched with the value of n_1 and n_2?

	Series	n_1	n_2	Region
(i)	Lyman	1	2, 3, ...	Ultraviolet
(ii)	Balmer	2	3, 4, ...	Infrared
(iii)	Paschen	3	4, 5, ...	Infrared
(iv)	Pfund	4	5, 6, ...	Infrared

(a) (i) and (ii) (b) (i) and (iii)
(c) (ii) and (iv) (d) (i) and (iv)

31. What is the colour corresponding to the wavelength of light emitted when the electron in a hydrogen atom undergoes transition from $n = 4$ to $n = 2$?

(a) Blue (b) Red
(c) Yellow (d) Green

SECTION - IV

Matching List Type

This section contains 3 multiple choice questions. Each question has matching lists. The codes for the lists have choices (a), (b), (c) and (d), out of which ONLY one is correct.

32. Match the List I with List II and select the correct answer using the code given below the lists.

	List I	List II
P.	Mass of H_2 produced when 0.5 mole of zinc reacts with excess of HCl	1. 3.01×10^{23} molecules
Q.	Mass of a molecule of a compound with formula $C_{70}H_{22}$	2. 6.023×10^{23} molecules
R.	Number of molecules in 35.5 g of Cl_2	3. 1.43×10^{-21} g
S.	Number of molecules in 64 g of SO_2	4. 1 g

	P	Q	R	S
(a)	2	1	4	3
(b)	1	2	3	4
(c)	4	3	1	2
(d)	4	3	2	1

33. Match the List I with List II for singly ionized helium atom if total energy of electron in first orbit in H-atom is –13.6 eV atom^{-1} and select the correct answer using the code given below the lists.

	List I	List II
P.	*P.E.* of electron in ground state	1. –54.4 eV atom^{-1}
Q.	*K.E.* of electron in ground state	2. +13.6 eV atom^{-1}
R.	Total energy of in ground state	3. –108.8 eV atom^{-1}
S.	Ionization energy of He^+ in lowest excited state	4. +54.4 eV atom^{-1}

	P	Q	R	S
(a)	1	2	3	4
(b)	4	1	2	3
(c)	4	2	1	3
(d)	3	4	1	2

34. Match the List I with List II and select the correct answer using the code given below the lists.

	List I	List II
P.	Isotopes	1. Same number of atoms and same number of valence electrons
Q.	Isobars	2. Different numbers of protons but same number of neutrons
R.	Isotones	3. Different numbers of protons and same number of neutrons and protons
S.	Isosters	4. Same number of protons but different numbers of neutrons

	P	Q	R	S
(a)	2	1	4	3
(b)	1	2	3	4
(c)	4	3	1	2
(d)	4	3	2	1

SECTION - V

Assertion-Reason Type

In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :

(a) If both assertion and reason are true and reason is the correct explanation of assertion.
(b) If both assertion and reason are true but reason is not the correct explanation of assertion.
(c) If assertion is true but reason is false.
(d) If both assertion and reason are false.

35. **Assertion :** The number of electrons ejected from a metal surface depends upon the frequency of light.
Reason : There is a time lag between the striking of light beam and the ejection of electrons from the metal surface.

36. **Assertion :** 12 parts by mass of carbon in CO and CO_2 molecules combine with 16 and 32 parts by mass of oxygen.
Reason : A given compound always contains exactly the same proportion of elements by weight.

37. **Assertion :** In case of isoelectronic ions the ionic size increases with the increase in atomic number.
Reason : The greater the attraction of nucleus, greater is the ionic radius.

38. **Assertion :** The greater the number of significant figures in a reported result, smaller is the uncertainty and greater is the precision.
Reason : A significant figure includes all the digits that are known with certainty plus one more digit which is estimated or is uncertain.

39. **Assertion :** Energy of the orbitals increases as $1s < 2s = 2p < 3s = 3p < 3d < 4s = 4p = 4d = 4f <$.....
Reason : Energy of the electron depends completely on principal quantum number.

40. **Assertion :** In a gaseous reaction, the ratio by volumes of reactants and gaseous products is in agreement with their molar ratio.
Reason : Volume of gas is inversely proportional to its number of moles at particular temperature and pressure.

SECTION - VI

Integer Value Correct Type

This section contains 10 questions. The answer to each question is a single digit integer, ranging from 0 to 9 (both inclusive).

41. Number of component values (in terms of $\frac{h}{2\pi}$) of orbital angular momentum along the z-direction for a $2p$ electron is

42. The vapour density of a mixture containing NO_2 and N_2O_4 is 38.3 at 27 °C. Moles of NO_2 in 100 g of mixture are $x \times 10^{-1}$. Value of x is

43. The degeneracy of hydrogen atom that has the energy equal to $-\frac{R_H}{9}$ is

44. A student performs a titration with different burettes and finds titre values of 25.2 mL, 25.25 mL, and 25.0 mL. The number of significant figures in the average titre value is

45. The frequency of radiation emitted when electron falls from $n = 4$ to $n = 1$ in H atom will be $x \times 10^{15}$ s^{-1}. The value of x is

46. A sample of pure Cu (3.18 g) heated in a stream of oxygen for sometime gains weight with the formation of black oxide of copper (CuO). The final weight is 3.92 g. The percentage of copper that remains unoxidised is approximately

47. When a certain metal was irradiated with light of frequency 3.2×10^{16} Hz, the photoelectrons emitted had twice the kinetic energy as did photoelectrons emitted when the same metal was irradiated with light of frequency 2.0×10^{16} Hz. The value of υ_0 for the metal is $x \times 10^{15}$ Hz. The value of x is

48. 1 mole of potassium chlorate is thermally decomposed and excess of aluminiun is burnt in the gaseous product. Number of moles of aluminium oxide formed is

49. Number of radial nodes present in $4d$ orbital is

50. The amount of water that should be added to 500 mL of 0.5 N solution of NaOH to give a concentration of 10 mg per mL is $x \times 10^2$ mL. The value of x is

SOLUTIONS

1. (d) : Number of atoms in 5 g of NH_3

$$= \frac{5}{17} \times 4 = 1.176\, N_A$$

Number of atoms in 11 g of CO_2

$$= \frac{11}{44} \times 3 = 0.75\, N_A$$

Number of atoms in 8 g of SO_2

$$= \frac{8}{64} \times 3 = 0.375\, N_A$$

Number of atoms in 4 g of $H_2 = \frac{4}{2} \times 2 = 4.00\, N_A$

2. (c): Let relative abundance of Cl-37 = x%
then relative abundance of Cl-35 = (100 – x)%
Average atomic mass

$$= \frac{x \times 37 + (100 - x)35}{100} = 35.5$$

$\Rightarrow$ $37x + 3500 - 35x = 3550$

$\Rightarrow$ $x = 25$

$\therefore$ $100 - x = 75$

Thus, the ratio of Cl-37 and Cl-35 is $x : (100 - x)$

$= 25 : 75 = 1 : 3$

3. (b) : Zeros between two non-zero digits are significant.

4. (d) : Since 13.6 eV is needed for ionization, 20.4 eV must have been absorbed. Of this, 6.8 eV is converted to kinetic energy. The velocity of the electrons is calculated as follows:

6.8 eV = 6.8 (1.60 × 10^{-19} C) (1 V) = 1.09 × 10^{-18} J

$$K.E. = \frac{1}{2}mv^2$$

$$\Rightarrow v = \sqrt{\frac{2K.E.}{m}} = \sqrt{\frac{2(1.09)\times 10^{-18}\ \text{J}}{9.109\times 10^{-31}\ \text{kg}}} = 1.55 \times 10^6\ \text{m/s}$$

According to the de Broglie equation

$$\lambda = \frac{h}{mv} = \frac{6.63\times 10^{-34}\ \text{J s}}{(9.109\times 10^{-31}\ \text{kg})(1.55\times 10^6\ \text{m/s})}$$

$$= 4.70 \times 10^{-10}\ \text{m}$$

5. (a) : Quantity of iron in one molecule

$$= \frac{67200}{100} = \times 0.334 = 224.45\ \text{amu}$$

No. of iron atoms in one molecule of haemoglobin $= \frac{224.45}{56} = 4$

6. (b) : Let no. of electrons in the ion $M^{3+} = x$

$\therefore$ No. of neutrons = $x + \frac{30.4x}{100} = 1.304x$

No. of electrons in the neutral atom = $x + 3$

$\therefore$ No. of protons = $x + 3$

Mass no. = No. of protons + No. of neutrons

$56 = x + 3 + 1.304x$ or $2.304x = 53$

or $x = 23$

No. of protons = $x + 3 = 23 + 3 = 26$

Hence the ion is $^{56}_{26}Fe^{3+}$.

7. (d) : Let the valency of metal be y and mol. wt. of metal be M.

$\therefore$ $2M + 60y$ is the weight of $M_2(CO_3)_y$ (metal carbonate) and $2M + 16y$ is the weight of M_2O_y (metal oxide).

1 g of metal carbonate gives 0.56 g of metal oxide

$\therefore$ $2M + 60y$ g of metal carbonate gives

(0.56) $(2M + 60y)$ g of metal oxide.

According to given condition,

$(0.56)\ (2M + 60y) = 2M + 16y \Rightarrow 17.6y = 0.88\, M$

$$\Rightarrow \frac{M}{y} = \text{equivalent wt. of metal} = 20$$

8. (d) : $\Delta x \cdot \Delta p = \frac{h}{4\pi}$ or $\Delta p = \frac{h}{4\pi} \cdot \frac{1}{\Delta x} = \frac{h}{0} = \infty$

9. (b) : Law of multiple proportions states that 'if two elements can combine to form more than one compound, the mass of one element that combines with a fixed mass of the other element, is in the ratio of small whole numbers.

10. (b) : Electronic configuration for Z = 105 [Rn] $5f^{14}6d^37s^2$, $n + l = 8$ for $5f$ (5 + 3 = 8) and for $6d$ (6 + 2 = 8). Electrons present in $5f$ = 14 and electrons present in $6d$ = 3. Total = 17

11. (b) : 100 mL of 1 M $AgNO_3$ = 0.1 mol $AgNO_3$
100 mL of 1 M $CuSO_4$ = 0.1 mol $CuSO_4$

$2AgNO_3 + H_2S \rightarrow Ag_2S + 2HNO_3$

2 moles 1 mol

0.1 mol 0.05 mol

$$\underset{1\text{ mol}}{CuSO_4} + \underset{1\text{ mol}}{H_2S} \rightarrow CuS + H_2SO_4$$
$$0.1\text{ mol} \quad 0.1\text{ mol}$$

∴ Ratio of the amounts of H_2S required
$= 0.05 : 0.1 = 1 : 2$

12. (d) : Cl^- and K^+ are isoelectronic species having same number of electrons (= 18). Greater the nuclear charge of an ion, more will be force of attraction for same number of electrons. K^+ has greater nuclear charge than Cl^- so attractive pull exerted by the nucleus is more and the size is smaller in K^+ ion.

13. (c): Let the formula of iron chloride be $FeCl_x$

$$\underset{(56 + 35.5\,x)\text{ g}}{FeCl_x} + x AgNO_3 \rightarrow \underset{143.5x\text{ g}}{x AgCl} + Fe(NO_3)_x$$

$$\frac{\text{wt. of } FeCl_x}{\text{wt. of AgCl}} = \frac{\text{mol. wt. of } FeCl_x}{\text{mol wt. of AgCl } (x \text{ unit})}$$

$$\frac{134.8}{304.8} = \frac{56 + 35.5x}{143.5x}$$

$\Rightarrow x = 2$

Hence, iron chloride is $FeCl_2$.

14. (a) : $n = 3$, $l = (n - 1) = 2$ *i.e.*, (0, 1, 2)
$m = -l$ to $+l$ (including 0)
∴ $m_l = -3$ (not possible)

15. (c): 18 mL H_2O = 18 g H_2O = 1 mol
$= 6.02 \times 10^{23}$ molecules
As there are ten electrons in H_2O, Avogadro's number should be multiplied with 10.
$= 10 \times 6.02 \times 10^{23}\ e^- = 6.02 \times 10^{24}\ e^-$

16. (c): Number of spherical nodes = $n - l - 1$
Number of non-spherical nodes = l
n and l are principal and azimuthal quantum numbers respectively. For 3*p*-orbital, $n = 3$, $l = 1$.
Thus, number of spherical nodes = 3 – 1 – 1 = 1 and number of non-spherical nodes = 1

17. (b) :
$$\underset{2\text{ g}}{H_2} + \underset{71\text{ g}}{Cl_2} \rightarrow \underset{73\text{ g}}{2HCl}$$

2 g of H_2 reacts with 71 g of Cl_2

100 g of H_2 will react with $\frac{71}{2} \times 100 = 3550$ g of Cl_2

Hence, Cl_2 is the limiting reagent.

71 g of Cl_2 produces 73 g of HCl

100 g of Cl_2 will produce $\frac{73}{71} \times 100$
$= 102.8$ g of HCl

18. (a) : The number of photoelectrons emitted from the surface of the metal is directly proportional to the intensity of the incident light.

19. (c): Molarity$(M) = \frac{\text{No. of moles of solute}}{\text{Volume of solution (in L)}}$

or, Molarity $= \frac{W_B \times 1000}{M_B \times \text{Volume of solution (in mL)}}$

$= \frac{5.85 \times 1000}{58.5 \times 500}$ (∵ Molar mass of NaCl $= 58.5$ g mol^{-1})

$= 0.2$ mol L^{-1}

20. (a) : Time taken to complete one revolution

$$t = \frac{\text{Circumference}}{\text{Velocity}} = \frac{2\pi r}{v}$$

We know, $mvr = \frac{nh}{2\pi}$

$$v = \frac{nh}{2\pi mr}$$

Thus, $t = \frac{2\pi r \times 2\pi mr}{nh} = \frac{4\pi^2 mr^2}{nh}$

21. (b, d) : $_{15}P^{32}$ total nucleons = $15p + 17n = 32$
$_{16}S^{32}$ total nucleons = $16p + 16n = 32$

22. (b, c) :

	A	*B*
Atomic weight	20	40
	1 mol	1 mol

Suppose 10 g of *A* = 1/2 mol of *A* = 1/2 mol of *B* = 20 g of *B* = 2*x* g of *B*
Hence, *x* g of *A* and 2*x* g of *B* will contain same number of atoms.
Suppose 11.2 L of *A*

$= \frac{1}{2}$ mol of $A = \frac{1}{2}$ mol of *B*

$= 11.2$ L of *B*

Hence, at STP, *x* L of *A* = *x* L of *B*
(All gases amounts same volume at STP)

x L of $A = y$ g

Suppose 11.2 mL of $A = \frac{1}{2}$ mol of A = 10 g of A

Now, 10 g of $B = \frac{1}{4}$ mol of B = 5.6 L at STP

$$= \frac{x}{2} \text{ L of } B \text{ at STP}$$

23. (d) : When intensity is doubled, number of electrons emitted per second is also doubled but average energy of photoelectrons emitted remains the same.

24. (b, c) : 1.0 g of $Mg = \frac{1}{12}$

$$= 0.0833 \text{ equivalent of Mg}$$

$$\left[\because \text{ Gram equivalent} = \frac{\text{Mass in g}}{\text{Equivalent mass}}\right]$$

0.5 g of $O_2 = \frac{0.5}{8} = 0.0625$ equivalent of O_2

O_2 is limiting reactant in the reaction to produce MgO.

$$\underset{1 \text{ mole}}{Mg} + \underset{1/2 \text{ mole}}{\frac{1}{2}O_2} \rightarrow \underset{1 \text{ mole}}{MgO}$$

Equivalent of O_2 = Equivalent of MgO

25. (a, b)

26. (a) : Weight of carbon = 12 × moles of CO_2

$$= \frac{12 \times 0.44}{44} = 0.12 \text{ g}$$

Weight of hydrogen = 2 × moles of H_2O

$$= \frac{2 \times 0.18}{18} = 0.02 \text{ g}$$

Weight of oxygen = 0.30 – (0.12 + 0.02) = 0.16 g

	C	H	O
Weight ratio	0.12	0.02	0.16
Mole ratio	$\frac{0.12}{12} = 0.01$	$\frac{0.02}{1} = 0.02$	$\frac{0.16}{16} = 0.01$

Simple ratio = 1 : 2 : 1

Empirical formula = CH_2O

Molecular weight = (Empirical formula weight)$_n$

$\Rightarrow$ 60 = $(30)_n \Rightarrow n = 2$

$\therefore$ Molecular formula = $C_2H_4O_2$

27. (b) : The molecular formula of the acid = (empirical formula)$_n$. Where 'n' is an integer. Therefore the molecular formula = CH_2O_2, here n = 1. The other molecular formulae do not fit the above equation.

28. (c):

Element	Weight ratio	Atomic mass	Molar ratio	Simplest ratio
Carbon	9	12	$\frac{9}{12} = 0.75$	3
Hydrogen	1	1	$\frac{1}{1} = 1$	4
Nitrogen	3.5	14	$\frac{3.5}{14} = 0.25$	1

$\therefore$ Empirical formula of the compound = C_3H_4N

$n\,(12 \times 3 + 1 \times 4 + 14 \times 1) = 108$

or, $n\,(36 + 4 + 14) = 108$

or, $54n = 108$

or, $n = 2$

$\therefore$ Molecular formula of the compound = $C_6H_8N_2$

29. (c)

30. (c): (ii) Balmer, $n_1 = 2$; $n_2 = 3, 4$; region - visible

(iv) Pfund, $n_1 = 5$; $n_2 = 6, 7$; region - infrared

31. (a) : $\frac{1}{\lambda} = R\left[\frac{1}{n_1^2} - \frac{1}{n_2^2}\right] = 109677\left[\frac{1}{2^2} - \frac{1}{4^2}\right] \text{ cm}^{-1}$

$$= 20564.4 \text{ cm}^{-1}$$

$$\lambda = \frac{1}{20564.4 \text{ cm}^{-1}} = 486 \times 10^{-7} \text{ cm}$$

or 486×10^{-9} m

Colour corresponding to this wavelength is blue.

32. (c): (P) : $Zn + 2HCl \longrightarrow ZnCl_2 + H_2$

1 mole of Zn produces 2 g of H_2

0.5 mole of Zn will produce 1 g of H_2

(Q) : $C_{70}H_{22}$

Gram molecular mass = 862 g

Mass of one molecule = $862/6.023 \times 10^{23}$ g

$= 1.43 \times 10^{-21}$ g

(R) : 71 g of $Cl_2 = 6.023 \times 10^{23}$ molecules
35.5 g of $Cl_2 = 3.01 \times 10^{23}$ molecules
(S) : Molar mass of $SO_2 = 64 = 1$ mole
64 g of $SO_2 = 6.023 \times 10^{23}$ molecules

33. (d) : $E_n = -\dfrac{13.6\,Z^2}{n^2}$ eV atom^{-1}

(P) For He^+, $Z = 2$; for ground state of He^+, $n = 1$
Hence, $E_1 = -13.6 \times 2^2 = -54.4$ eV atom^{-1}
But $E_1 = P.E. + K.E.$

$$= P.E. - \frac{P.E.}{2} = \frac{P.E.}{2} = -54.4 \text{ eV atom}^{-1}$$

$\Rightarrow$ $P.E. = -108.8$ eV atom^{-1}

(Q) $K.E. = -\dfrac{P.E.}{2} = -\dfrac{-(-108.8)}{2} = +54.4$ eV atom^{-1}

(R) $E_1 = E_{total} = -54.4$ eV atom^{-1}

(S) For ionization of 1st excited state of He^+, $n_1 = 2$, $n_2 = \infty$

Hence, $I.E. = \Delta E = 13.6 \times Z^2 \left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right]$

$$= 13.6 \times 2^2 \left[\frac{1}{2^2} - \frac{1}{\infty^2}\right]$$

$$= +13.6 \text{ eV atom}^{-1}$$

34. (d) : (P) Isotopes have same atomic number and hence same number of protons but different mass numbers and hence different number of neutrons.
(Q) Isobars have different atomic numbers and hence different number of protons and same mass number and hence same number of neutrons and protons.
(R) Isotones have same number of neutrons but have different mass number and hence different number of protons.
(S) Isosters are molecules containing same number of atoms and same number of valence electrons (*e.g.* CO_2 and N_2O).

35. (d) : The number of electrons ejected is proportional to the intensity or brightness of light and the electrons are ejected from the metal surface as soon as the beam of light strikes.

36. (b) : The masses of oxygen (*i.e.* 16 g and 32 g) which combine with a fixed mass of carbon (*i.e.* 12 g) bear a simple ratio, *i.e.* 16 : 32 or 1 : 2. This is in accordance with the law of multiple proportions.

37. (d) : In case of isoelectronic ions the size decreases with increase in atomic number and greater the attraction of nucleus smaller is the ionic radius.

38. (a) : Precision refers to the closeness of the set of values obtained from identical measurements of a quantity. Significant figures are the meaningful digits in a measured or calculated quantity.

40. (d) : Energy of electron depends on both 'n' and 'l' hence the order given in assertion is totally wrong as per $(n + l)$ rule. However, exception to this is H and H-related species, which are very few.

40. (c): Volume of gas is directly proportional to its number of moles at particular temperature and pressure.

41. (3) : The component values of orbital angular momentum in z-direction = $m_l \times \dfrac{h}{2\pi}$

and values of m_l for $2p$ is $-1, 0, +1$.
So, number of component values is 3.

42. (7) : Mixture contains NO_2 and N_2O_4
Molar mass of $NO_2 = 46$ with % = x
Molar mass of $N_2O_4 = 92$ with % = $(100 - x)$
Molar mass of mixture = $38.3 \times 2 = 76.6$ g mol^{-1}

$$\therefore \quad 76.6 = \frac{M_1x_1 + M_2x_2}{x_1 + x_2}$$

$$= \frac{46x + 92(100 - x)}{100}$$

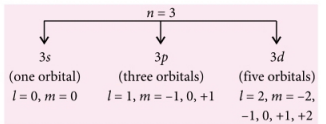
$\Rightarrow$ $7660 = 46x + 9200 - 92x$
$\Rightarrow$ $x = 33.47$
$\Rightarrow$ $NO_2 = 33.47$ g

$$\text{Moles of } NO_2 = \frac{33.47}{46} = 0.728$$

$\Rightarrow$ $7.28 \times 10^{-1} \approx 7 \times 10^{-1}$
Thus, $x = 7$.

43. (9) : Energy in hydrogen atom is given as

$$-\frac{R_H}{n^2}=-\frac{R_H}{9} \Rightarrow n=3$$



Hence, degeneracy = 1 + 3 + 5 = 9

44. (3) : Average titre value $=\frac{25.2+25.25+25.0}{3}$

$= 25.15$

According to rounding off rule of significant figures, if the right most digit to be removed is 5, then the preceding number is not changed if it is even; but increased by one, if it is odd.

$\therefore$ 25.15 can be rounded off to 25.2 and has three significant figures.

45. (3) : $\Delta E = E_4 - E_1 = \frac{hc}{\lambda} = h\upsilon$

$$\therefore \upsilon=\frac{E_4-E_1}{h}=\frac{-21.76\times10^{-19}\left[\frac{1}{4^2}-\frac{1}{1^2}\right]}{6.625\times10^{-34}}$$

$$\left[E_n=\frac{-21.76\times10^{-19}}{n^2}\right]$$

$= 3.079 \times 10^{15}\ s^{-1} \approx 3 \times 10^{15}\ s^{-1}$

46. (8) : 63.6 g of Cu gives (63.6 + 16) g of CuO

So, a g of Cu will give $\frac{(63.6+16)}{63.6}a$ g of CuO

Thus, final weight

$$=(3.18-a)+\frac{(63.6+16)a}{63.6}=3.92$$

$a = 2.94$ g

Thus, % of Cu left unoxidised

$$=\frac{(3.18-2.94)}{3.18}\times100\approx8\%$$

47. (8) : $K.E. = h\upsilon - h\upsilon_0$ or $\upsilon - \upsilon_0 = \frac{K.E.}{h}$

Given, $K.E._2 = 2K.E._1$

$$\upsilon_2-\upsilon_0=\frac{K.E._2}{h} \quad \ldots \text{(i)}$$

and $$\upsilon_1-\upsilon_0=\frac{K.E._1}{h} \quad \ldots \text{(ii)}$$

Dividing equation (i) by equation (ii),

$$\frac{\upsilon_2-\upsilon_0}{\upsilon_1-\upsilon_0}=\frac{K.E._2}{K.E._1}=\frac{2K.E._1}{K.E._1}=2$$

or $\upsilon_2 - \upsilon_0 = 2\upsilon_1 - 2\upsilon_0$

or $\upsilon_0 = 2\upsilon_1 - \upsilon_2 = 2(2.0 \times 10^{16}) - (3.2 \times 10^{16})$

$= 8.0 \times 10^{15}$ Hz

48. (1) : $2KClO_3 \rightarrow 2KCl + 3O_2$

$4Al + 3O_2 \rightarrow 2Al_2O_3$

2 moles of $KClO_3$ gives 3 moles of O_2 (gaseous product).

$\therefore$ 1 mole of $KClO_3$ gives 3/2 moles of O_2.

Also, 3 moles of O_2 (gaseous product) give 2 moles of Al_2O_3.

$\therefore$ $\frac{3}{2}$ moles of O_2 will give $=\frac{2}{3}\times\frac{3}{2}$

$= 1$ mole of Al_2O_3

49. (1) : Number of radial nodes = $(n - l - 1)$

For $4d$ orbital, $n = 4$ and $l = 2$

$\therefore$ Number of radial nodes = 4 – 2 – 1 = 1

50. (5) : Concentration = 10 mg mL^{-1} = 10 g L^{-1}

$$=\frac{10}{40}\ \text{N}=0.25\ \text{N}$$

$N_1V_1 = N_2V_2$,

i.e., $0.5 \times 500 = 0.25 \times V_2$

or $V_2 = 1000$ mL

$\therefore$ Volume of water to be added

$= 1000 - 500$ mL $= 500$ mL $= 5 \times 10^2$ mL

$\therefore$ $x = 5$

2015 CBSE-BOARD

CHAPTERWISE PRACTICE PAPER

Series-1

The Solid State | Solutions

Time : 3 hrs. Marks : 70

GENERAL INSTRUCTIONS

(i) All questions are compulsory.
(ii) Question numbers 1 to 8 are very short-answer questions and carry 1 mark each.
(iii) Question numbers 9 to 18 are short-answer questions and carry 2 marks each.
(iv) Question numbers 19 to 27 are also short-answer questions and carry 3 marks each.
(v) Question numbers 28 to 30 are long-answer questions and carry 5 marks each.
(vi) Use Log Tables, if necessary. Use of calculator is not allowed.

1. Name one solid which shows both Frenkel and Schottky defects.

2. Give an example of solution showing negative deviation from ideal behaviour.

3. How many atoms can be assigned to its unit cell if an element forms (i) body-centred cubic unit cell and (ii) a face-centred cubic unit cell?

4. What is the effect of temperature on (i) Molarity (ii) Molality ?

5. What are F-centres? Mention one property which is caused due to the presence of F-centres.

6. State Henry's law about the solubility of a gas in a liquid.

7. Why is glass considered as supercooled liquid?

8. Solutions *A*, *B*, *C* and *D* are respectively 0.1 M glucose, 0.05 M NaCl, 0.05 M $BaCl_2$ and 0.1 M $AlCl_3$. Which solutions are isotonic ?

9. What is the simplest formula of a solid whose cubic unit cell has the atom *A* at each corner, the atom *B* at each face centre and a *C* atom at the body centre?

10. Calculate the boiling point of a solution containing 0.61 g of benzoic acid in 50 g of carbon disulphide assuming 84% dimerisation of the acid. The boiling point and K_b of CS_2 are 46.2 °C and 2.3 K kg mol^{-1} respectively.

11. Calculate the efficiency of packing in case of a metal crystal for simple cubic.

12. With the help of a suitable diagram show that the lower vapour pressure of a solution than the pure solvent causes a lowering of freezing point for the solution compared to that of the pure solvent.

13. How would you account for the following?
(i) Schottky defects lower the density of related solids.
(ii) Impurity doped silicon is a semiconductor.

14. What is the molar concentration of solute particle in human blood if the osmotic pressure is 7.2 atm at the body temperature of 37 °C?
[$R = 0.0821$ L atm K^{-1}]

15. What are the differences between crystalline and amorphous solids?

16. Explain:

(i) Ionic crystals are hard and brittle.

(ii) Vacancies are introduced in an ionic solid when a cation of higher valence is added as an impurity in it.

17. Potassium has a *bcc* structure with nearest neighbour distance 4.52 Å. Its atomic weight is 39. What will be its density?

18. Define the term, 'osmosis'. What is the advantage of using osmotic pressure as compared to other colligative properties for the determination of molar masses of solutes in solutions?

OR

Show graphically how the vapour pressure of a solvent and its solution containing a non-volatile solute change with temperature. Show on this graph the boiling points of the solvent and the solution. Which is higher and why?

19. On dissolving 19.5 g of CH_2FCOOH in 500 g of water, a depression of 1 °C in freezing point of water is observed. Calculate the van't Hoff factor and dissociation constant of fluoroacetic acid. Given $K_f = 1.86$ K kg mol^{-1}

20. Explain the following properties giving suitable examples:

(i) Ferromagnetism

(ii) Paramagnetism

21. A sample of drinking water was found to be severely contaminated with chloroform ($CHCl_3$) supposed to be a carcinogen. The level of contamination was 15 ppm (by mass).

(i) Express this in percentage by mass.

(ii) Determine the molality of chloroform in the water sample.

22. Li crystallises in *bcc* structure. If the edge length of unit cell is 353 pm, calculate (i) radius of Li atom, (ii) packing efficiency of unit cell.

23. Explain the following terms:

(i) Semiconductor

(ii) *n*-type semiconductor

(iii) *p*-type semiconductor

OR

How will you distinguish between the following pairs of terms?

(i) Hexagonal close packing and cubic close packing.

(ii) Crystal lattice and Unit cell.

(iii) Tetrahedral void and octahedral void.

24. Calculate the mole fraction of ethylene glycol ($C_2H_6O_2$) in a solution containing 20% of $C_2H_6O_2$ by mass.

25. Metallic gold crystallises in a *fcc* lattice and has a density of 19.3 g cm^{-3}. Calculate the radius of gold atom.

26. An owner of a sweet shop asked his newly appointed servant to arrange Laddu's in a tray keeping layer over layers. The servant arranged laddus by keeping them in parallel pattern. As soon as he took the tray in his hand, the laddus fell down except the first layer.

(i) Why did laddus fall?

(ii) How Laddus should be arranged?

(iii) What value is shown by this?

27. On the basis of band theory explain the difference between a conductor, an insulator and a semiconductor with the help of suitable diagrams.

28. (i) Two elements *A* and *B* form compounds having molecular formula AB_2 and AB_4. When dissolved in 20 g of benzene (C_6H_6), 1 g of AB_2 lowers the freezing point by 2.3 K whereas 1.0 g of AB_4 lowers it by 1.3 K. The molal depression constant for benzene is 5.1 K kg mol^{-1}. Calculate atomic masses of *A* and *B*.

(ii) What do you understand by 'colligative properties'? Write them.

OR

(i) Define azeotrope and explain briefly minimum boiling azeotrope by taking suitable example.

(ii) The vapour pressures of pure liquids *A* and *B* are 450 mm of Hg and 700 mm of Hg respectively at 350 K. Calculate the composition of liquid mixture if total

vapour pressure is 600 mm of Hg. Also find the composition of the mixture in vapour phase.

29. (i) Atoms of element *B* form *hcp* lattice and those of the element *A* occupy 2/3rd of tetrahedral voids. What is the formula of the compound formed by these elements *A* and *B*?

(ii) Analysis shows that nickel oxide has formula $Ni_{0.98}O_{1.00}$. What fractions of the nickel exist as Ni^{2+} and Ni^{3+} ions?

OR

(i) A compound is formed by two elements *M* and *N*. The element *N* forms *ccp* and atoms of *M* occupy 1/3rd of tetrahedral voids. What is the formula of the compound?

(ii) Ferric oxide crystallises in a hexagonal close packed array of oxide ions with two out of every three octahedral holes occupied by ferric ions. Derive the formula of the ferric oxide.

30. (i) State Raoult's law for solutions of volatile liquids. Explain the meaning of positive and negative deviations from Raoult's law. Also give examples.

(ii) Vapour pressure of chloroform ($CHCl_3$) and dichloromethane (CH_2Cl_2) at 298 K are 200 mm Hg and 415 mm Hg respectively. Calculate the vapour pressure of the solution prepared by mixing 25.5 g of $CHCl_3$ and 40 g of CH_2Cl_2 at 298 K.

OR

(i) Define the term osmotic pressure. Describe how the molecular mass of a substance can be determined by a method based on measurement of osmotic pressure.

(ii) At 300 K, 36 g of glucose $C_6H_{12}O_6$ present per litre in its solution has an osmotic pressure of 4.98 bar. If the osmotic pressure of another solution is 1.52 bar at the same temperature, calculate the concentration of the other solution.

SOLUTIONS

1. AgBr

2. Water and sulphuric acid solution shows negative deviation from ideal behaviour.

3. (i) 2, (ii) 4

4. (i) Molarity decreases with the increase in temperature.

(ii) Molality does not change with temperature.

5. The anionic sites occupied by unpaired electrons in a solid having metal excess defect are called F-centres. F-centres impart characteristic colour to the compound.

6. Henry's law states that the solubility of a gas in a liquid is directly proportional to the pressure of the gas.

7. Glass is an amorphous solid and it has tendency to flow very slowly like liquids.

8. Solutions *A* and *B* are isotonic as they have equal molar concentrations of particles.

9. Contribution of atoms *A* towards the unit cell $= 8 \times \frac{1}{8} = 1$

Contribution of atoms *B* towards the unit cell $= 6 \times \frac{1}{2} = 3$

Contribution of atoms *C* towards the unit cell = 1

Hence, the formula of the solid is AB_3C.

10.

$$C_6H_5COOH \rightleftharpoons (C_6H_5COOH)_2$$

	1 mol	0
Initial		
After association	$1-\alpha$	$\alpha/2$

$$\text{Total} = 1-\alpha+\frac{\alpha}{2} = 1-\frac{\alpha}{2}$$

$$i = 1-\frac{\alpha}{2} = 1-\frac{0.84}{2} = 1-0.42 = 0.58$$

$$\Delta T_b = iK_b m = 0.58 \times 2.3 \times \frac{0.61}{122} \times \frac{1000}{50} = 0.1334\ ^\circ C$$

$$\therefore \quad T_{solution} = 46.2 + 0.1334 = 46.3334\ ^\circ C$$

11. There is only one atom per unit cell in simple cubic unit cell, so volume occupied by one atom $= \frac{4}{3}\pi r^3$.

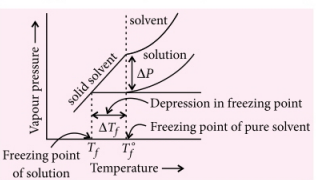
Volume of unit cell $= a^3 = (2r)^3 = 8r^3$

Efficiency of packing

$$= \frac{\text{Volume occupied by atoms}}{\text{Volume of the unit cell}}$$

$$= \frac{4/3\pi r^3}{8r^3} = \frac{\pi}{6} = 0.5233 \text{ or } 52.33\%$$

12. Figure shows how the lowering of vapour pressure of a solution causes lowering of its freezing point as compared to pure solvent.



13. **(i)** Schottky defects occur when equal number of cations and anions are missing from their lattice site. Mass of unit cell decreases which further decreases the density of the solid.

(ii) The conductivity of intrinsic semiconductor like silicon is too low to be of practical use hence the conductivity is increased by adding an appropriate amount of suitable impurity like Al or As which is electron deficient or electron rich.

14. Given, $\pi = 7.2$ atm, $R = 0.0821$ L atm K^{-1}

$T = 37\ °C = 273 + 37 = 310$ K

$$\pi = \frac{n}{V}RT$$

$$\Rightarrow \quad \pi = CRT \qquad \left[C = \frac{n}{V}\right]$$

$$\Rightarrow \quad 7.2 = C \times 0.0821 \times 310$$

$$\Rightarrow \quad C = \frac{7.2}{0.0821 \times 310} \Rightarrow C = \frac{7.2}{25.451}$$

$C = 0.283$ mol L^{-1}

15.

	Crystalline solid	Amorphous solid
1.	They have well defined geometrical shape.	They have irregular shape.
2.	They have sharp melting point.	They gradually soften over a range of temperature.
3.	They are anisotropic.	They are isotropic.
4.	They have definite and characteristic heat of fusion.	They do not have definite heat of fusion.

16. **(i)** Ionic crystals are hard due to the presence of strong interionic electrostatic forces of attraction.
However, when an ionic solid is subjected to stress, ions of same charge come close together and the repulsive forces between them cause the crystal to break into pieces. Thus, ionic crystals are hard but brittle.

(ii) When a cation of higher valence is added as an impurity in an ionic solid then to maintain electrical neutrality two or more cations of lower valency are replaced. One position is occupied by added cation and other creates vacancies in the lattice.

17. For *bcc*, $d = \frac{\sqrt{3}}{2}a$

$$\text{or} \quad a = \frac{2d}{\sqrt{3}} = \frac{2 \times 4.52}{1.732} = 5.219\ \text{Å} = 522\ \text{pm}$$

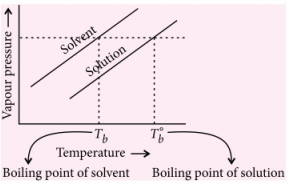
$$\rho = \frac{Z \times M}{a^3 \times N_A \times 10^{-30}}$$

$$= \frac{2 \times 39}{(522)^3 \times (6.02 \times 10^{23}) \times 10^{-30}}$$

$$= 0.91\ \text{g/cm}^3 = 910\ \text{kg m}^{-3}$$

18. The net spontaneous flow of the solvent molecules from the solvent to the solution or from a less concentrated solution to more concentrated solution through a semi-permeable membrane is called osmosis.
The osmotic pressure method has the advantage over other methods as pressure measurement is around the room temperature and its magnitude is large even for very dilute solution.

OR



From this graph it is obvious that boiling point of solution in higher than that of pure solvent because vapour pressure of solution is lower than that of the vapour pressure of solvent.

19. Given $W_A = 19.5$ g, $W_B = 500$ g, $K_f = 1.86$ K kg mol^{-1}, $\Delta T_f = 1$ °C

$$\Delta T_f = \frac{K_f \times W_B \times 1000}{M_B \times W_A}$$

$$M_B = \frac{K_f \times W_B \times 1000}{\Delta T_f \times W_A}$$

$$= \frac{1.86 \text{ K kg mol}^{-1} \times 19.5 \text{ g} \times 1000}{1.0 \text{ K} \times 500 \text{ g}}$$

$$= 72.54 \text{ g mol}^{-1}$$

Molecular mass of CH_2FCOOH

$$= 12 + 2 + 19 + 12 + 32 + 1 = 78 \text{ g mol}^{-1}$$

$$i = \frac{\text{Normal molecular mass}}{\text{Observed molecular mass}} = \frac{78}{72.54} = 1.0753$$

$$\underset{C \text{ mol L}^{-1}}{CH_2FCOOH} \rightleftharpoons \underset{0}{CH_2FCOO^-} + \underset{0}{H^+}$$

$$\underset{C(1-\alpha)}{} \qquad \underset{C\alpha}{} \qquad \underset{C\alpha}{}$$

$$\alpha = \frac{i-1}{n-1} = i - 1 = 1.0753 - 1 = 0.0753 \quad (\because n = 2)$$

$$K_a = \frac{[CH_2FCOO^-][H^+]}{[CH_2FCOOH]} = \frac{(C\alpha)^2}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

$$C = \frac{19.5 \times 1000}{78 \times 500} = 0.5 \text{ M}$$

$$K_a = C\alpha^2 = 0.5 \times (0.0753)^2 = 2.83 \times 10^{-3}$$

20. (i) Materials which are strongly attracted by magnetic field and show permanent magnetism even in the absence of the magnetic field are called ferromagnetic materials and the property thus exhibited is called ferromagnetism.
e.g., Fe, Co, Ni show ferromagnetism at room temperature.

(ii) Substances which are weakly attracted by a magnetic field are called paramagnetic substances and the property is called paramagnetism.
e.g., O_2, S_2, Cu^{2+}, Mn^{2+}, etc.

21. (i) 15 ppm means 15 parts present in million (10^6) parts by mass of the solution

$$\% \text{ by mass} = \frac{15}{10^6} \times 100 = 1.5 \times 10^{-3}$$

(ii) Mass of solvent = 10^6 g
(Mass of solute is negligible)
Molar mass of $CHCl_3 = 12 + 1 + 3 \times 35.5$
$= 119.5$ g mol^{-1}
Number of moles of $CHCl_3$

$$= \frac{\text{Mass in g}}{\text{Molar mass}} = \frac{15}{119.5}$$

$$\therefore \quad \text{Molality} = \frac{15/119.5}{10^6} \times 1000$$

$$= 1.25 \times 10^{-4} \text{ m}$$

22. (i) Given structure = *bcc*, $a = 353$ pm, $r = ?$
For *bcc* structure

$$r = \frac{\sqrt{3}\,a}{4} = \frac{1.732 \times 353 \text{ pm}}{4} = 152.85 \text{ pm}$$

(ii) Structure = *bcc*, $a = 353$ pm $= 353 \times 10^{-12}$ m
Packing efficiency of *bcc* unit cell

$$= \frac{Z \times \frac{4}{3}\pi r^3}{a^3}$$

$$= \frac{2 \times \frac{4}{3} \times 3.14 \times (152.85 \times 10^{-12} \text{ m})^3}{(353 \times 10^{-12} \text{ m})^3} = 0.68$$

$$= 68\%$$

23. (i) The solids which have conductivities between 10^{-6} to 10^{4} ohm^{-1} m^{-1} are called semiconductors.

e.g. Germanium and silicon.

(ii) When group-14 elements like silicon is doped with atoms of group-15 elements, such as P, As, Sb or Bi then only four of the five valence electrons of each impurity atom participate in forming covalent bonds and fifth electron is almost free to conduct electricity. Such type of semiconductor is called *n*-type semiconductor.

(iii) When group-14 elements like silicon is doped with atoms of group-13 elements, such as B, Al, Ga or In then each impurity atom forms only three covalent bonds with the host atom. The place where the fourth electron is missing is called a hole which moves through the crystal like a positive charge and hence increases its conductivity. Such type of semiconductor is called *p*-type semiconductor.

OR

(i) In hexagonal close packing, third layer is built by covering tetrahedral voids of second layer and spheres of the third layer are exactly aligned with those of the first layer (*ABAB*, …pattern).

In cubic close packing third layer is built by covering octahedral voids of second layer and spheres in fourth layer are aligned with those of the first layer (*ABCABC* … pattern).

(ii) Crystal lattice is regular three dimensional arrangement of constituent particles of a crystal.

Unit cell is the smallest portion of a crystal lattice which when repeated in different directions generates the entire lattice.

(iii) A simple triangular void surrounded by four spheres is called tetrahedral void. A double triangular void surrounded by six spheres is called octahedral void.

24. Let total mass of solution = 100 g

$\therefore$ Mass of ethylene glycol $w_2 = 20$ g

and mass of solvent (water) = $w_1 = 80$ g

Molar mass of $C_2H_6O_2$, M_2

$= 12 \times 2 + 1 \times 6 + 16 \times 2$

$= 62$ g mol^{-1}

Molar mass of H_2O, $M_1 = 1 \times 2 + 16$

$= 18$ g mol^{-1}

Moles of H_2O; $n_1 = \dfrac{w_1}{M_1} = \dfrac{80}{18} = 4.444$ mol

Moles of $C_2H_6O_2$; $n_2 = \dfrac{w_2}{M_2} = \dfrac{20}{62} = 0.322$ mol

Mole fraction of $C_2H_6O_2 = \dfrac{n_2}{n_1 + n_2}$

$= \dfrac{0.322}{4.44 + 0.322} = \dfrac{0.322}{4.766} = 0.068$

25. Given, structure = *fcc*

$\therefore$ $Z = 4$, $d = 19.3$ g cm^{-3}, $r = ?$

$M = 197$ amu $= 197$ g mol^{-1},

$N_A = 6.023 \times 10^{23}$ mol^{-1}

Using formula, $d = \dfrac{Z \times M}{N_A \times a^3}$ or $a^3 = \dfrac{Z \times M}{d \times N_A}$

or $a^3 = \dfrac{4 \times 197\ \text{g mol}^{-1}}{19.3\ \text{g cm}^{-3} \times 6.022 \times 10^{23}\ \text{mol}^{-1}}$

$a^3 = 67.799 \times 10^{-24}$ cm^3.

$\therefore$ $a = 4.08 \times 10^{-8}$ cm

For *fcc* lattice $r = \dfrac{a}{2\sqrt{2}} = \dfrac{408\ \text{pm}}{2 \times 1.414} = 144.3$ pm

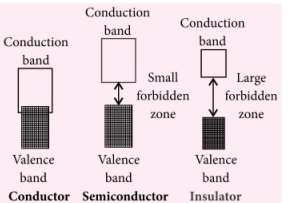
26. (i) Parallel arrangement of spheres is quite inefficient packing.

(ii) Laddus should be arranged in hexagonal close packing in all the layers.

(iii) Skill is more important than labour.

27. In a conductor, valence band and conduction band overlap with each other.

In a semiconductor, there is small forbidden zone between the two.



In an insulator, there is a large forbidden zone between the two.

28. (i) Applying the formula,

$$M_2 = \frac{1000 \times K_f \times w_2}{w_1 \times \Delta T_f}$$

$$M_{AB_2} = \frac{1000 \times 5.1 \times 1}{20 \times 2.3} = 110.87\,\text{g mol}^{-1}$$

$$M_{AB_4} = \frac{1000 \times 5.1 \times 1}{20 \times 1.3} = 196.15\,\text{g mol}^{-1}$$

Suppose atomic masses of A and B are 'a' and 'b' respectively. Then

Molar mass of $AB_2 = a + 2b$
$= 110.87\ \text{g mol}^{-1}$ … (i)

Molar mass of $AB_4 = a + 4b$
$= 196.15\ \text{g mol}^{-1}$ … (ii)

Eqn. (ii) – Eqn. (i) gives $2b = 85.28$

or $b = 42.64$

Substituting in eqn. (i) we get

$a + 2 \times 42.64 = 110.87$

or $a = 25.59$

Thus, atomic mass of $A = 25.59$ u

Atomic mass of $B = 42.64$ u

(ii) Those properties of solution which depend upon the number of solute particles and not upon the nature of the solute particles are known as colligative properties.

There are four colligative properties

(I) Relative lowering of vapour pressure

(II) Elevation of boiling point (ΔT_b)

(III) Depression of freezing point (ΔT_f)

(IV) Osmotic pressure (π)

OR

(i) Azeotrope is a liquid mixture which boils at constant temperature without undergoing change in composition.

e.g., A mixture of 95% ethanol and 5% water by mass forms minimum boiling azeotrope as for this composition vapour pressure is maximum and boiling point is minimum. It boils at a temperature lower than expected and shows positive deviation from ideal behaviour.

(ii) $p_A^\circ = 450$ mm Hg, $p_B^\circ = 700$ mm Hg

$p_{\text{total}} = p_A^\circ x_A + p_B^\circ x_B$

$600 = 450(x_A) + 700\,(1 - x_A)$

On solving

$x_A = 0.4$, $x_B = 0.6$

In vapour phase (Using Dalton's law)

$p_A = 0.4 \times 450$ mm $= 180$ mm Hg

$p_B = 0.6 \times 700$ mm $= 420$ mm Hg

$$x'_A = \frac{180\ \text{mm}}{600\ \text{mm}} = 0.3;\ x'_B = \frac{420\ \text{mm}}{600\ \text{mm}} = 0.7$$

29. (i) Number of atoms $B = 6$

Tetrahedral voids $= 2 \times 6 = 12$

$$\therefore \text{ Number of atoms } A = \frac{2}{3} \times 12 = 8$$

So, the formula of compound is A_8B_6 *i.e.* A_4B_3.

(ii) $Ni_{0.98}O_{1.00}$;

Let Ni^{2+} be 'x' and Ni^{3+} will be $0.98 - x$

Total charge on compound is equal to zero

$\therefore \quad +2x + 3(0.98 - x) - 2 = 0$

$+2x + 2.94 - 3x - 2 = 0$

$x = 0.94$

$$\%\ \text{of } Ni^{2+} = \frac{0.94}{0.98} \times 100 = 96\% \text{ and}$$

$\%$ of $Ni^{3+} = 4\%$

OR

(i) Number of N atoms in *ccp* arrangement

$$= 8 \times \frac{1}{8} = 1$$

M occupies $\frac{1}{3}$ rd of tetrahedral voids

Total number of voids $= 2 \times N$

$$\Rightarrow \text{ Total number of } M = 2 \times \frac{1}{3} = \frac{2}{3}$$

$$M : N \Rightarrow \frac{2}{3} : 1 \Rightarrow 2 : 3$$

$\therefore$ Formula is M_2N_3.

(ii) Number of oxide ions forming *hcp* = 6
Number of octahedral voids = 6

$$\text{Number of ferric ions} = \frac{2}{3} \times 6 = 4$$

$\therefore$ Formula of ferric oxide is Fe_4O_6 *i.e.*, Fe_2O_3.

30. (i) Raoult's law states that for a solution of volatile liquids, the partial vapour pressure of each component of the solution is directly proportional to its mole fraction present in solution.
Thus, for components 1 and 2

$$p_1 \propto x_1, \qquad p_2 \propto x_2$$

and $p_1 = p_1^\circ x_1, \quad p_2 = p_2^\circ x_2$

where p_1° and p_2° are the vapour pressures of pure components 1 and 2 at the same temperature.
If partial vapour pressures of the components are higher than the value calculated from Raoult's law, the solution exhibits positive deviation.
In this case, the intermolecular attractive forces between the solute-solvent molecules are weaker than those between the solute-solute and solvent-solvent molecules and leads to increase in vapour pressure. *e.g.*, mixture of ethanol and acetone.
If partial vapour pressures of the components are lower than the value calculated from Raoult's law, the solution exhibits negative deviation.
In this case, the intermolecular attractive forces between solute-solute and solvent-solvent are weaker than those between solute-solvent and leads to decrease in vapour pressure. *e.g.*, mixture of phenol and aniline.

(ii) Molar mass of CH_2Cl_2
$= 12 \times 1 + 1 \times 2 + 35.5 \times 2$
$= 85 \text{ g mol}^{-1}$
Molar mass of $CHCl_3$
$= 12 \times 1 + 1 \times 1 + 35.5 \times 3$
$= 119.5 \text{ g mol}^{-1}$

$$\text{Moles of } CH_2Cl_2 = \frac{40 \text{ g}}{85 \text{ g mol}^{-1}} = 0.47 \text{ mol}$$

$$\text{Moles of } CHCl_3 = \frac{25.5 \text{ g}}{119.5 \text{ g mol}^{-1}} = 0.213 \text{ mol}$$

Total number of moles = 0.47 + 0.213
= 0.683 mol

$$x_{CH_2Cl_2} = \frac{0.47}{0.683} = 0.688$$

$$p_{total} = p_1^\circ + (p_2^\circ - p_1^\circ)\, x_2$$
$$= 200 + (415 - 200) \times 0.688$$
$$= 200 + 147.9 = 347.9 \text{ mm Hg}$$

OR

(i) Osmotic pressure of the solution is the pressure that just stops the flow of solvent from its side to solution side across a semi-permeable membrane.

$$\pi V = nRT$$

$$\pi V = \frac{w_B}{M_B} RT$$

$$\Rightarrow \quad M_B = \frac{w_B \times R \times T}{\pi \times V}$$

(ii) $$\pi(\text{glucose}) = \frac{n}{V} RT$$

$$= \frac{w_1}{M_1 V} RT$$

$$4.98 = \left(\frac{36}{180 \times 1}\right) RT = 0.2\, RT \qquad \ldots \text{(i)}$$

$$\pi(\text{unknown}) = \frac{w_2}{V \times M_2} RT = M' RT$$

$[\because M' = \text{Molarity}]$

$$1.52 = M' RT \qquad \ldots \text{(ii)}$$

By dividing eqn. (ii) by (i),

$$\therefore \quad \frac{1.52}{4.98} = \frac{M' RT}{0.2\, RT}$$

$$\therefore \quad M' = 0.2 \times \frac{1.52}{4.98} = 0.061 \text{ M}$$

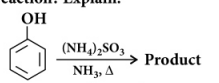
YOU ASKED WE ANSWERED

Do you have a question that you just can't get answered?

Use the vast expertise of our mtg team to get to the bottom of the question. From the serious to the silly, the controversial to the trivial, the team will tackle the questions, easy and tough.

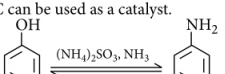
The best questions and their solutions will be printed in this column each month.

Q1. What will be the product formed in the given reaction? Explain.

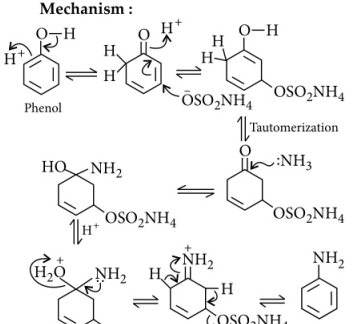


– Saumik Dey, Jalpaiguri, West Bengal

Ans. Transformation of phenol into aniline using ammonium sulphite at 150 °C is called *Bucherer reaction*. In this reaction, $ZnCl_2$ at 300 °C can be used as a catalyst.



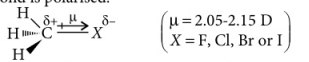
Mechanism :



Q2. Why are alkyl halides insoluble in water, though they are polar in nature?

– Navdeep Kumar, Amritsar, Punjab

Ans. In an alkyl halide, the halogen atom is bonded to sp^3-hybridized carbon atom. As the halogen is more electronegative than carbon, the C—*X* bond is polarised.

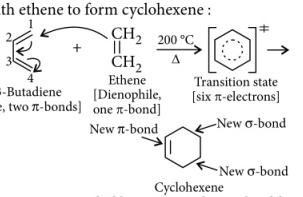


Due to polar nature of alkyl halides, they are held together by strong dipole-dipole interactions. The new forces of attraction between alkyl halide and water are not enough to overcome alkyl halide-alkyl halide (dipole-dipole) and water-water (hydrogen bonding) forces of attraction. Hence, alkyl halides are immiscible with water.

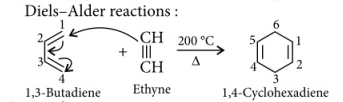
Q3. What is Diels–Alder reaction?

–Saumik Dey, Jalpaiguri, West Bengal

Ans. In Diels–Alder reaction, a conjugated diene reacts with an alkene to produce a six-membered ring containing one π-bond *i.e.* cycloalkene. Hence, this reaction is also known as *cycloaddition reaction* because the reaction forms a cyclic product, *via* a cyclic transition state. *e.g.* Reaction of 1,3-butadiene with ethene to form cyclohexene :



Even, alkynes can also serve as dienophiles in Diels–Alder reactions :



Diels–Alder reaction is a *concerted reaction*, in which all the electrons move at the same time. ■■

NCERT CORNER

CLASS XI-XII

The questions given in this column have been prepared strictly on the basis of NCERT Chemistry. Last year JEE (Main & Advanced) / AIPMT / AIIMS / other PMTs have drawn their papers heavily from NCERT books. Practise hard ! All the best !!

1. Which one of the following compounds is most reactive towards S_N1 reaction?
(a) $C_6H_5CH(C_6H_5)Br$
(b) $C_6H_5CH(CH_3)Br$
(c) $C_6H_5C(CH_3)(C_6H_5)Br$
(d) $C_6H_5CH_2Br$

2. A first order reaction, which is 30% complete in 30 minutes has a half-life period of
(a) 102.2 min. (b) 58.2 min.
(c) 24.2 min. (d) 120.2 min.

3. Which of the following compounds has least oxidation state of Fe?
(a) $K_3[Fe(OH)_6]$
(b) $K_2[FeO_4]$
(c) $FeSO_4{\cdot}(NH_4)_2SO_4{\cdot}6H_2O$
(d) $[Fe(CN)_6]^{3-}$

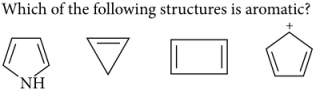
4. Hyperconjugation is not possible in
(a) $CH_3-CH=CH_2$
(b) $CH_2=CH_2$
(c) 
(d) $(CH_3)_2C=C(CH_3)_2$

5. The mass of a photon with a wavelength equal to 1.54×10^{-8} cm is
(a) 0.8268×10^{-34} kg (b) 1.2876×10^{-33} kg
(c) 1.4285×10^{-32} kg (d) 1.8884×10^{-32} kg

6. Cannizzaro reaction is not given by
(a) acetaldehyde
(b) formaldehyde
(c) benzaldehyde
(d) trimethylacetaldehyde.

7. Schottky defect in crystals is observed when
(a) unequal number of cations and anions are missing from the lattice site
(b) equal number of cations and anions are missing from the lattice site
(c) an ion leaves its normal site and occupies an interstitial site
(d) density of the crystal is increased.

8. Which of the following structures is aromatic?



I II III IV

(a) I and II only (b) I only
(c) II only (d) III only

9. Which of the following is an ore of potassium?
(a) Carnallite (b) Cryolite
(c) Bauxite (d) Dolomite

10. Match the coordination compounds given in column I with the central metal atoms given in column II and assign the correct code:

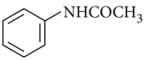
Column I		Column II	
(i)	Chlorophyll	(p)	Rhodium
(ii)	Blood pigment	(q)	Cobalt
(iii)	Wilkinson catalyst	(r)	Iron
(iv)	Vitamin B_{12}	(s)	Magnesium

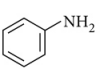
	(i)	(ii)	(iii)	(iv)
(a)	(p)	(q)	(s)	(r)
(b)	(s)	(q)	(r)	(p)
(c)	(s)	(r)	(p)	(q)
(d)	(q)	(r)	(s)	(p)

11. The most nucleophilic nitrogen is in

(a) 

(b) 

(c) 

(d) 

12. Most favourable conditions for ionic bonding are
(a) low charge on ions, large cation, large anion
(b) low charge on ions, large cation, small anion
(c) high charge on ions, large cation, small anion
(d) high charge on ions, small cation, large anion.

13. In the following reaction,
$4P + 3KOH + 3H_2O \longrightarrow 3KH_2PO_2 + PH_3$
(a) P is only oxidised
(b) P is only reduced
(c) P is both oxidised as well as reduced
(d) None of these.

14. Which of the following salts of H_3PO_3 exists?
(I) NaH_2PO_3 (II) Na_2HPO_3
(III) Na_3PO_3
(a) I and II only (b) I, II and III
(c) II and III only (d) III only

15. The glucose is an example of
(a) disaccharide
(b) aldohexose
(c) ketohexose
(d) non-reducing sugar.

16. In which of the following pairs, the ionization enthalpy of the first species is less than that of the second?
(a) N, P (b) Be^+, Be
(c) N, N^- (d) S, P

17. What is '*Z*' in the following sequence of reactions?

$$\text{Phenol} \xrightarrow[\text{Dust}]{\text{Zn}} X \xrightarrow[\text{Anhyd. } AlCl_3]{CH_3Cl} Y \xrightarrow[KMnO_4]{\text{Alkaline}} Z$$

(a) Benzene (b) Toluene
(c) Benzaldehyde (d) Benzoic acid

18. Which of the following is not a resonating structure for the phenoxide ion?

(I) 

(II) 

(III) 

(IV) 

(a) I (b) II
(c) III (d) IV

19. The equilibrium constant of the reaction:

$$SO_{3(g)} \rightleftharpoons SO_{2(g)} + \frac{1}{2}O_{2(g)}$$

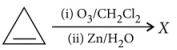
is 0.15 at 900 K. The equilibrium constant for $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ is
(a) 52.52 mol^{-1} L (b) 49.72 mol^{-1} L
(c) 63.34 mol^{-1} L (d) 44.44 mol^{-1} L

20. Permanent hardness of water can be removed by
(a) sodium sulphate
(b) sodium bicarbonate
(c) washing soda
(d) sodium chloride.

21. The final product obtained on heating ethanoic acid with P_2O_5 is
(a) ethene (b) ethanoic anhydride
(c) ethane (d) methyl acetate.

22. Graphite is a good conductor of electricity because it
(a) has sp^2-hybridized carbon atoms
(b) has free electrons
(c) is crystalline
(d) has free atoms.

23. Final product '*X*' of the following reaction is



(a) 1, 3-propanedial
(b) 1, 3-propanedioic acid
(c) ethanal
(d) formaldehyde.

24. The standard reduction potential for two reactions are given below:

(i) $AgCl + e^- \longrightarrow Ag_{(s)} + Cl^-_{(aq)}; E° = 0.22$ V

(ii) $Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}$; $E° = 0.80$ V

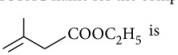
The solubility product of AgCl under standard conditions of temperature is given by

(a) 1.613×10^{-5} (b) 1.535×10^{-8}
(c) 3.213×10^{-10} (d) 1.477×10^{-10}

25. Standard entropies of X_2, Y_2 and XY_3 are 60, 30 and 50 J K^{-1} mol^{-1} respectively. For the reaction $1/2X_2 + 3/2Y_2 \rightleftharpoons XY_3$, $\Delta H = -30$ kJ, to be at equilibrium, the temperature should be

(a) 750 K (b) 1000 K
(c) 1250 K (d) 500 K

26. The IUPAC name for the compound



is

(a) ethyl acrylate
(b) ethyl methacrylate
(c) ethyl-2-methylbut-2-enoate
(d) ethyl-3-methylbut-3-enoate.

27. The correct order of electron affinity of B, C, N and O is

(a) O > C > N > B (b) B > N > C > O
(c) O > C > B > N (d) O > B > C > N

28. Cumene process is the most important commercial method for the manufacture of phenol. Cumene is

(a) 1-methyl ethyl benzene
(b) ethyl benzene
(c) vinyl benzene
(d) propyl benzene.

29. Which one of the following statements concerning lanthanides elements is false?

(a) Lanthanides are separated from one another by ion exchange methods.
(b) The ionic radii of trivalent lanthanides steadily increase with increase in atomic number.
(c) All lanthanides are highly dense metals.
(d) Most characteristic oxidation state of lanthanides elements is +3.

30. Select the correct option, among Sc(III), Ti(IV), Pd(II) and Cu(II) ions.

(a) All are paramagnetic.
(b) All are diamagnetic.
(c) Sc(III), Ti(IV) are paramagnetic and Pd(II), Cu(II) are diamagnetic.
(d) Sc(III), Ti(IV) are diamagnetic and Pd(II), Cu(II) are paramagnetic.

31. Maximum number of molecules are present in

(a) 7 g N_2 (b) 2 g H_2
(c) 16 g NO_2 (d) 16 g O_2

32. The average velocity and the most probable velocity of gas molecules are expressed as

(a) $\left(\frac{8RT}{M}\right)^{1/2}, \frac{8RT}{\pi M}$ (b) $\left(\frac{3RT}{M}\right)^{1/2}, \frac{2RT}{M}$

(c) $\left(\frac{8RT}{\pi M}\right)^{1/2}, \left(\frac{2RT}{M}\right)^{1/2}$

(d) $\left(\frac{8RT}{\pi M}\right), \left(\frac{3RT}{M}\right)^{1/2}$

33. Which of the following statements is false?

(a) Photochemical smog causes irritation in eyes.
(b) London smog is a mixture of smoke and fog.
(c) Photochemical smog results in the formation of PAN.
(d) London smog is oxidising in nature.

34. Which of the following noble gases is not present in atmosphere?

(a) He (b) Ne
(c) Ar (d) Rn

35. An emulsion is formed when

(a) a gas is dispersed in a liquid
(b) a gas is dispersed in a solid
(c) a liquid is dispersed in a gas
(d) a liquid is dispersed in a liquid.

36. The chemical reagent used for leaching of gold and silver ores is
(a) sodium hydroxide
(b) potassium cyanide
(c) potassium cyanate
(d) sodium thiosulphate.

37. Major product obtained when anisole undergoes Friedel–Crafts alkylation
(a) 2-methoxytoluene
(b) 2-methoxyacetophenone
(c) 4-methoxytoluene
(d) 4-methoxyacetophenone.

38. The highest lattice energy corresponds to
(a) MgO (b) CaO
(c) SrO (d) BaO

39. Which one of the following is reduced with zinc and hydrochloric acid to give the corresponding hydrocarbon?
(a) Ethyl acetate (b) Acetic acid
(c) Acetamide (d) Butan-2-one

40. On heating with soda-lime, salicylic acid gives
(a) phenol (b) benzoic acid
(c) sodium salicylate (d) benzene.

41. When a non-volatile substance is dissolved in a solvent, the vapour pressure of the solvent is decreased. This results in
(a) an increase in the boiling point of the solution
(b) a decrease in the boiling point of the solvent
(c) the solution having a higher freezing point than the solvent
(d) the solution having a lower osmotic pressure than the solvent.

42. Pick out the wrong statement(s).
(i) Vapour pressure of a liquid is the measure of the strength of intermolecular attractive forces.
(ii) Surface tension of a liquid acts perpendicular to the surface of the liquid.
(iii) Vapour pressure of all liquids is same at their freezing points.
(iv) Liquids with stronger intermolecular attractive forces are more viscous than those with weaker intermolecular force.
(a) (ii), (iii) and (iv) (b) (ii) and (iii)
(c) (i), (ii) and (iii) (d) (iii) only

43. Which of the following species cannot work as oxidizing agent?
(a) O_2 (b) $KMnO_4$
(c) H_2O_2 (d) I^-

44. Crystal field stabilization energy for high spin d^4 octahedral complex is
(a) $-1.8\,\Delta_o$ (b) $-1.6\,\Delta_o + P$
(c) $-1.2\,\Delta_o$ (d) $-0.6\,\Delta_o$

45. Benzene hexachloride is a/an
(a) antiseptic (b) insecticide
(c) catalyst (d) analgesic.

46. Which of the following is a condensation polymer?
(a) Teflon (b) Dacron
(c) Polystyrene (d) Neoprene

47. Uncertainty in position of an electron (mass = 9.1×10^{-28} g) moving with a velocity of 3×10^4 cm/s accurate upto 0.001% will be (Use $h/4\pi$) in uncertainty expression where $h = 6.626 \times 10^{-27}$ erg-second)
(a) 5.76 cm (b) 7.68 cm
(c) 1.93 cm (d) 3.84 cm.

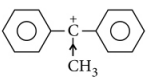
48. In the reaction $A + B \longrightarrow$ products, on doubling the concentration of A, keeping that of B constant the reaction rate is doubled. However, when the initial concentrations of both A and B are doubled the rate is increased eight times. The rate of the given reaction is, therefore
(a) $k[A]^2$ (b) $k[A]^2[B]^2$
(c) $k[A][B]^2$ (d) $k[A]^2[B]$

49. The oxidation number of phosphorus and basicity of acid in pyrophosphoric acid respectively are
(a) + 4 and three (b) + 1 and four
(c) + 5 and four (d) + 3 and one.

50. An aqueous solution of borax is
(a) neutral (b) acidic
(c) basic (d) amphoteric.

SOLUTIONS

1. (c) : S_N1 reactions proceed via the formation of a carbocation intermediate.
More stable is the carbocation more reactive is the alkyl/aryl halide towards S_N1 reaction.
In $C_6H_5C^+(CH_3)(C_6H_5)$ carbocation, the two phenyl rings by their $-R$ effect and $—CH_3$ by its $+I$ effect diminish the positive charge and make it stable.



2. (b) : For first order reaction

$$t = \frac{2.303}{k}\log\frac{a}{a-x}$$

$$\frac{t_{30\%}}{t_{50\%}} = \frac{\frac{2.303}{k}\log\frac{100}{100-30}}{\frac{2.303}{k}\log\frac{100}{100-50}}$$

$$\frac{30}{t_{1/2}} = \frac{\log\frac{10}{7}}{\log 2}$$

$$\frac{30}{t_{1/2}} = \frac{0.1549}{0.3010}$$

$$t_{1/2} = \frac{0.3010\times 30}{0.1549} = 58.2 \text{ min.}$$

3. (c) : In $K_3[Fe(OH)_6]$, O.N. of Fe = +3
In $K_2[FeO_4]$, O.N. of Fe = +6
In $FeSO_4\cdot(NH_4)_2SO_4\cdot 6H_2O$, O.N. of Fe = +2
In $[Fe(CN)_6]^{3-}$, O.N. of Fe = +3.

4. (b) : Hyperconjugation occurs through the H-atoms present on the carbon atom next to the double bond *i.e.*, α-hydrogen atoms.

5. (c) : Mass of photon, $m = \frac{h}{\lambda v}$

$$= \frac{6.6\times 10^{-34}\text{ J s}}{1.54\times 10^{-10}\text{ m}\times 3\times 10^{8}\text{ ms}^{-1}}$$

$$= 1.4285\times 10^{-32}\text{ kg}$$

6. (a) : Acetaldehyde does not undergo Cannizzaro reaction since it contains α-H atoms while formaldehyde, trimethylacetaldehyde and benzaldehyde undergo Cannizzaro reaction since they do not contain α-H atoms.

7. (b) : It is a stoichiometric defect in which equal number of cations and anions are missing from the lattice site.

8. (b) : Only I follows Huckel's rule and is aromatic.

9. (a) : Carnallite is $KCl\cdot MgCl_2\cdot 6H_2O$. All other ores do not contain K.

10. (c)

11. (a) : In option (b) lone pair of electrons on N is a part of aromaticity and in option (c) NH– group is adjacent to electron withdrawing group ($-COCH_3$) and in option (d) lone pair is a part of resonance. So, pyridine is most nucleophilic.

12. (b) : According to Fajan rules, formation of ionic bond is favoured by low charge on ions, large cation and small anion.

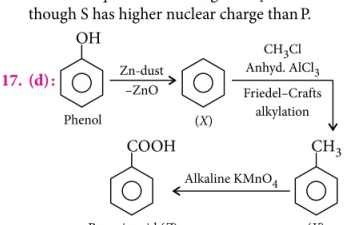
13. (c) : $\overset{0}{4P} + 3KOH + 3H_2O \rightarrow 3K\overset{+1}{H_2}P\overset{}{O_2} + \overset{-3}{P}H_3$
Here, O.N. of P increases from 0 in elemental P to + 1 in KH_2PO_2 and decreases to –3 in PH_3. Therefore, P is both oxidised as well as reduced.

14. (a) : H_3PO_3 is a dibasic acid so NaH_2PO_3 and Na_2HPO_3 both exist.

15. (b) : Glucose is an aldohexose as it contains 6 carbon atoms in its molecule and has an aldehydic group.

16. (d) : P because of extra stability of the exactly half-filled $3p$-orbitals has higher IE_1 than S even though S has higher nuclear charge than P.

17. (d) :



18. (d): Negative charge is never delocalized on the *meta* position.

19. (d): For $SO_{3(g)} \rightleftharpoons SO_{2(g)} + \frac{1}{2}O_{2(g)}$

$$K_{c_1} = \frac{[SO_2][O_2]^{1/2}}{[SO_3]} = 0.15 \quad \ldots (i)$$

For $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

$$K_{c_2} = \frac{[SO_3]^2}{[SO_2]^2[O_2]} \quad \ldots (ii)$$

By reversing Eq. (i), $\frac{1}{K_{c_1}} = \frac{[SO_3]}{[SO_2][O_2]^{1/2}}$

On making square,

$$\left(\frac{1}{K_{c_1}}\right)^2 = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = K_{c_2} \quad \text{[By Eq. (ii)]}$$

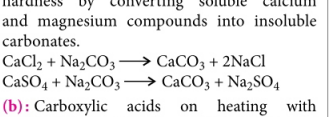
$$\therefore \quad K_{c_2} = \left(\frac{1}{0.15}\right)^2 = 44.44 \text{ mol}^{-1} \text{ L}$$

20. (c): Washing soda removes permanent hardness by converting soluble calcium and magnesium compounds into insoluble carbonates.

$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2NaCl$

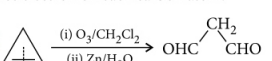
$CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3 + Na_2SO_4$

21. (b): Carboxylic acids on heating with dehydrating agents such as H_2SO_4 or P_2O_5 give corresponding anhydrides.



22. (b): Graphite shows moderate conductivity due to the presence of unpaired or free fourth valence electron on each carbon atom.

23. (a):



24. (d): On subtracting eqn (ii) from (i) we get

$AgCl_{(s)} \longrightarrow Ag^+ + Cl^-$,

$E^\circ_{cell} = 0.22 - 0.80 = -0.58$ V

Now, $E_{cell} = E^\circ_{cell} - \frac{0.059}{1}\log[Ag^+][Cl^-]$

At equilibrium $E_{cell} = 0$

Thus $E^\circ_{cell} = \frac{0.059}{1} \log [Ag^+][Cl^-]$

$$-0.58 = \frac{0.059}{1} \log [Ag^+][Cl^-]$$

$\therefore$ $\log [Ag^+] [Cl^-] = -9.8305$

or $\log K_{sp} = -9.8305$

$K_{sp} = 1.477 \times 10^{-10}$

25. (a): Given reaction is :

$$\frac{1}{2}X_2 + \frac{3}{2}Y_2 \rightleftharpoons XY_3$$

We know, $\Delta S^\circ = \Sigma S^\circ_{products} - \Sigma S^\circ_{reactants}$

$= 50 - (30 + 60)$

$= -40 \text{ J K}^{-1} \text{ mol}^{-1}$

At equilibrium $\Delta G^\circ = 0$

$\therefore$ $\Delta H^\circ = T\Delta S^\circ$

or $T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{-30 \times 10^3 \text{ J mol}^{-1}}{-40 \text{ J K}^{-1} \text{ mol}^{-1}} = 750 \text{ K}$

26. (d)

27. (c): Electron affinity increases from left to right in a period but for group 15 (nitrogen family) it is less due to stable half-filled electronic configuration. Thus order is O > C > B > N.

28. (a): Cumene is isopropyl benzene or 1-methyl ethyl benzene.

29. (b): The ionic radii of trivalent lanthanides steadily decrease with increase in atomic number (lanthanide contraction).

30. (d): $Sc^{3+}(3d^0)$, $Ti^{4+}(3d^0)$ are diamagnetic while $Pd^{2+}(4d^8)$ and $Cu^{2+}(3d^9)$ are paramagnetic.

31. (b): 1 mole of any element contains 6.023×10^{23} number of molecules.

1 g mol of O_2 = 32 g oxygen

$\Rightarrow$ 16 g of O_2 = 0.5 g mol O_2

1 g mol of N_2 = 28 g N_2

$\Rightarrow$ 7 g N_2 = 0.25 g mol N_2

1 g mol of H_2 = 2 g hydrogen

$\Rightarrow$ 2 g H_2 = 1.0 g mol H_2

1 g mol NO_2 = 14 + 16 × 2 = 46 g of NO_2

$\Rightarrow$ 16 g of NO_2 = 0.35 g mol NO_2

Hence, 2 g H_2 (1 g mol H_2) contain maximum number of molecules.

32. (c)

33. (d): London smog or sulphurous smog contains SO_2 and hence is reducing in nature.

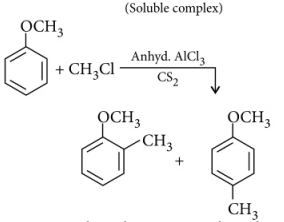
34. (d)

35. (d): Emulsion is a colloidal dispersion in which both the dispersed phase and the dispersion medium are liquids.

36. (b): $Ag_2S + 4KCN \longrightarrow \underset{\text{(Soluble complex)}}{2K[Ag(CN)_2]} + K_2S$

$4Au + 8KCN + 2H_2O + O_2 \longrightarrow \underset{\text{(Soluble complex)}}{4K[Au(CN)_2]} + 4KOH$

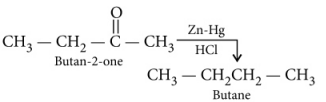
37. (c):



2-Methoxytoluene (Minor) 4-Methoxytoluene (Major)

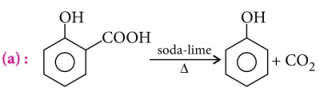
38. (a): Due to small size, MgO has highest lattice enegry.

39. (d): Butan-2-one will get reduced into butane when treated with zinc and hydrochloric acid following Clemmensen reduction reaction whereas Zn/HCl do not reduce ester, acid and amide.



Butan-2-one Butane

40. (a):



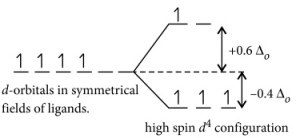
Salicylic acid Phenol

41. (a): The boiling point of a liquid is the temperature at which its vapour pressure is equal to the atmospheric pressure. The vapour pressure of a liquid is lowered when a non-volatile solute is added to it. Therefore, the temperature of the solution when its vapour pressure will be equal to atmospheric pressure will be higher than the temperature of pure solvent. Thus boiling point of a solution increases by addition of a non-volatile solute.

42. (d): Vapour pressures of all liquids are different at their freezing points.

43. (d): I^- can act as a reducing agent and not as an oxidising agent because its O.S. can change from –1 to +7 only.

44. (d): $-0.6\ \Delta_o$

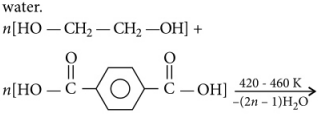


$CFSE = 3(-0.4)\Delta_o + 0.6\ \Delta_o = -1.2\ \Delta_o + 0.6\ \Delta_o$

$CFSE = -0.6\ \Delta_o$

45. (b): Benzene hexachloride sold under the name gammexane, which is an insecticide.

46. (b): Dacron is formed by condensation polymerization of ethylene glycol and terephthalic acid with the elimination of water.



47. (c): Mass of an electron (m) = 9.1×10^{-28} g;

Velocity of electron (v) = 3×10^4 cm/s ;

$$\text{Accuracy} = 0.001\% = \frac{0.001}{100} \text{ and}$$

Planck's constant (h) = 6.626×10^{-27} erg-second.

Actual velocity of the electron (Δv)

$$= 3 \times 10^4 \times \frac{0.001}{100} = 0.3 \text{ cm/s}$$

Therefore, uncertainty in the position of the electron

$$(\Delta x) = \frac{h}{4\pi m \Delta v} = \frac{6.626 \times 10^{-27}}{4\pi \times (9.1 \times 10^{-28}) \times 0.3}$$

$$= 1.93 \text{ cm}$$

48. (c): Let the rate law be, Rate = $k[A]^x\,[B]^y$ (i)

Now, $2 \times \text{Rate} = k[2A]^x\,[B]^y$ (ii)

$8 \times \text{Rate} = k[2A]^x\,[2B]^y$ (iii)

On dividing (iii) by (ii),

$$4 = \left(\frac{2B}{B}\right)^y \text{ or, } 4 = 2^y \Rightarrow y = 2$$

Divide (ii) by (i), we get

$$2 = \left(\frac{2A}{A}\right)^x \text{ or, } 2 = 2^x \Rightarrow x = 1$$

$\therefore$ Rate = $k[A]\,[B]^2$

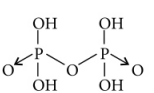
49. (c): Pyrophosphoric acid : $H_4P_2O_7$

Let Oxidation state of P be x

$\Rightarrow 4 \times (+1) + 2x + 7 \times (-2) = 0$

$\Rightarrow 4 + 2x - 14 = 0$

$\Rightarrow x = +5$



Basicity of acid is four.

50. (c): Borax dissolves in water to give alkaline solutions.

$$Na_2B_4O_7 + 7H_2O \longrightarrow \underset{\text{Strong base}}{2NaOH} + \underset{\text{Weak acid}}{4H_3BO_3}$$

SOLVED PAPER 2014

AIPMT

1. What is the maximum number of orbitals that can be identified with the following quantum numbers?
$n = 3, l = 1, m_l = 0$
(a) 1 (b) 2 (c) 3 (d) 4

2. Calculate the energy in joule corresponding to light of wavelength 45 nm. (Planck's constant, $h = 6.63 \times 10^{-34}$ Js, speed of light, $c = 3 \times 10^{8}$ ms^{-1})
(a) 6.67×10^{15} (b) 6.67×10^{11}
(c) 4.42×10^{-15} (d) 4.42×10^{-18}

3. Equal masses of H_2, O_2 and methane have been taken in a container of volume V at temperature 27 °C in identical conditions. The ratio of the volumes of gases $H_2 : O_2$: methane would be
(a) 8 : 16 : 1 (b) 16 : 8 : 1
(c) 16 : 1 : 2 (d) 8 : 1 : 2

4. If a is the length of the side of a cube, the distance between the body centered atom and one corner atom in the cube will be
(a) $\frac{2}{\sqrt{3}}a$ (b) $\frac{4}{\sqrt{3}}a$ (c) $\frac{\sqrt{3}}{4}a$ (d) $\frac{\sqrt{3}}{2}a$

5. Which property of colloids is not dependent on the charge on colloidal particles?
(a) Coagulation (b) Electrophoresis
(c) Electro-osmosis (d) Tyndall effect

6. Which of the following salts will give highest pH in water?
(a) KCl (b) NaCl
(c) Na_2CO_3 (d) $CuSO_4$

7. Of the following 0.10 m aqueous solutions, which one will exhibit the largest freezing point depression?
(a) KCl (b) $C_6H_{12}O_6$
(c) $Al_2(SO_4)_3$ (d) K_2SO_4

8. When 22.4 litres of $H_{2(g)}$ is mixed with 11.2 litres of $Cl_{2(g)}$, each at S.T.P, the moles of $HCl_{(g)}$ formed is equal to
(a) 1 mol of $HCl_{(g)}$ (b) 2 mol of $HCl_{(g)}$
(c) 0.5 mol of $HCl_{(g)}$ (d) 1.5 mol of $HCl_{(g)}$

9. When 0.1 mol MnO_4^{2-} is oxidised the quantity of electricity required to completely oxidise MnO_4^{2-} to MnO_4^{-} is
(a) 96500 C (b) 2 × 96500 C
(c) 9650 C (d) 96.50 C

10. Using the Gibb's energy change, $\Delta G° = +63.3$ kJ, for the following reaction,
$$Ag_2CO_{3(s)} \rightleftharpoons 2Ag^{+}_{(aq)} + CO^{2-}_{3(aq)}$$
the K_{sp} of $Ag_2CO_{3(s)}$ in water at 25 °C is
($R = 8.314$ J K^{-1} mol^{-1})
(a) 3.2×10^{-26} (b) 8.0×10^{-12}
(c) 2.9×10^{-3} (d) 7.9×10^{-2}

11. The weight of silver (at. wt. = 108) displaced by a quantity of electricity which displaces 5600 mL of O_2 at STP will be
(a) 5.4 g (b) 10.8 g (c) 54.0 g (d) 108.0 g

12. Which of the following statements is correct for the spontaneous adsorption of a gas?
(a) ΔS is negative and, therefore ΔH should be highly positive.
(b) ΔS is negative and therefore, ΔH should be highly negative.
(c) ΔS is positive and therefore, ΔH should be negative.
(d) ΔS is positive and therefore, ΔH should also be highly positive.

13. For the reversible reaction,
$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} + \text{heat}$
The equilibrium shifts in forward direction

(a) by increasing the concentration of $NH_{3(g)}$
(b) by decreasing the pressure
(c) by decreasing the concentrations of $N_{2(g)}$ and $H_{2(g)}$
(d) by increasing pressure and decreasing temperature.

14. For the reaction, $X_2O_{4(l)} \longrightarrow 2XO_{2(g)}$
$\Delta U = 2.1$ kcal, $\Delta S = 20$ cal K^{-1} at 300 K
Hence, ΔG is
(a) 2.7 kcal (b) −2.7 kcal
(c) 9.3 kcal (d) −9.3 kcal

15. For a given exothermic reaction, K_p and K_p' are the equilibrium constants at temperatures T_1 and T_2, respectively. Assuming that heat of reaction is constant in temperature range between T_1 and T_2, it is readily observed that
(a) $K_p > K_p'$ (b) $K_p < K_p'$
(c) $K_p = K_p'$ (d) $K_p = \frac{1}{K_p'}$

16. Which of the following orders of ionic radii is correctly represented?
(a) $H^- > H^+ > H$ (b) $Na^+ > F^- > O^{2-}$
(c) $F^- > O^{2-} > Na^+$ (d) $Al^{3+} > Mg^{2+} > N^{3-}$

17. 1.0 g of magnesium is burnt with 0.56 g O_2 in a closed vessel. Which reactant is left in excess and how much? (At. wt. Mg = 24, O = 16)
(a) Mg, 0.16 g (b) O_2, 0.16 g
(c) Mg, 0.44 g (d) O_2, 0.28 g

18. The pair of compounds that can exist together is
(a) $FeCl_3$, $SnCl_2$ (b) $HgCl_2$, $SnCl_2$
(c) $FeCl_2$, $SnCl_2$ (d) $FeCl_3$, KI

19. Be^{2+} is isoelectronic with which of the following ions?
(a) H^+ (b) Li^+ (c) Na^+ (d) Mg^{2+}

20. Which of the following molecules has the maximum dipole moment?
(a) CO_2 (b) CH_4 (c) NH_3 (d) NF_3

21. Which one of the following species has plane triangular shape?
(a) N_3 (b) NO_3^- (c) NO_2^- (d) CO_2

22. Acidity of diprotic acids in aqueous solutions increases in the order
(a) $H_2S < H_2Se < H_2Te$
(b) $H_2Se < H_2S < H_2Te$
(c) $H_2Te < H_2S < H_2Se$
(d) $H_2Se < H_2Te < H_2S$

23. (I) $H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$
(II) $H_2O_2 + Ag_2O \longrightarrow 2Ag + H_2O + O_2$
Role of hydrogen peroxide in the above reactions is respectively
(a) oxidizing in (I) and reducing in (II)
(b) reducing in (I) and oxidizing in (II)
(c) reducing in (I) and (II)
(d) oxidizing in (I) and (II)

24. Artificial sweetner which is stable under cold conditions only is
(a) saccharine (b) sucralose
(c) aspartame (d) alitame.

25. In acidic medium, H_2O_2 changes $Cr_2O_7^{2-}$ to CrO_5 which has two (—O—O—) bonds. Oxidation state of Cr in CrO_5 is
(a) +5 (b) +3 (c) +6 (d) −10

26. The reaction of aqueous $KMnO_4$ with H_2O_2 in acidic conditions gives
(a) Mn^{4+} and O_2 (b) Mn^{2+} and O_2
(c) Mn^{2+} and O_3 (d) Mn^{4+} and MnO_2.

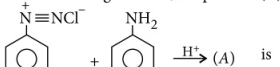
27. Among the following complexes the one which shows zero crystal field stabilization energy (CFSE) is
(a) $[Mn(H_2O)_6]^{3+}$ (b) $[Fe(H_2O)_6]^{3+}$
(c) $[Co(H_2O)_6]^{2+}$ (d) $[Co(H_2O)_6]^{3+}$

28. Magnetic moment 2.83 BM is given by which of the following ions?
(At. nos. Ti = 22, Cr = 24, Mn = 25, Ni = 28)
(a) Ti^{3+} (b) Ni^{2+} (c) Cr^{3+} (d) Mn^{2+}

29. Which of the following complexes is used to be as an anticancer agent?
(a) *mer*-$[Co(NH_3)_3Cl_3]$
(b) *cis*-$[PtCl_2(NH_3)_2]$
(c) *cis*-$K_2[PtCl_2Br_2]$
(d) Na_2CoCl_4

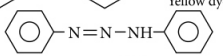
30. Reason of lanthanoid contraction is
(a) negligible screening effect of '*f*'-orbitals
(b) increasing nuclear charge
(c) decreasing nuclear charge
(d) decreasing screening effect.

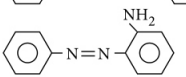
31. In the following reaction, the product (*A*)

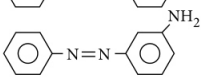


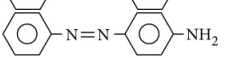
is

Yellow dye

(a) 

(b) 

(c) 

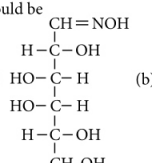
(d) 

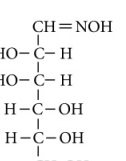
32. Which of the following will be most stable diazonium salt $RN_2^+X^-$?

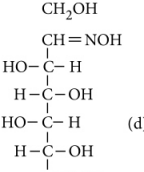
(a) $CH_3N_2^+X^-$ (b) $C_6H_5N_2^+X^-$

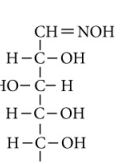
(c) $CH_3CH_2N_2^+X^-$ (d) $C_6H_5CH_2N_2^+X^-$

33. *D*(+)-glucose reacts with hydroxyl amine and yields an oxime. The structure of the oxime would be

(a) 

(b) 

(c) 

(d) 

34. Which of the following hormones is produced under the conditions of stress which stimulate glycogenolysis in the liver of human beings?

(a) Thyroxin (b) Insulin

(c) Adrenaline (d) Estradiol

35. Which one of the following is an example of thermosetting polymer?

(a) 

(b) 

(c) 

(d) 

36. Which of the following organic compounds polymerizes to form the polyester Dacron?

(a) Propylene and *para* HO—(C_6H_4)—OH

(b) Benzoic acid and ethanol

(c) Terephthalic acid and ethylene glycol

(d) Benzoic acid and *para* HO—(C_6H_4)—OH

37. Which one of the following is not a common component of Photochemical smog?

(a) Ozone

(b) Acrolein

(c) Peroxyacetyl nitrate

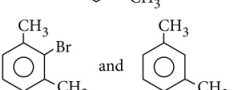
(d) Chlorofluorocarbons

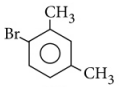
38. In the Kjeldahl's method for estimation of nitrogen present in a soil sample, ammonia evolved from 0.75 g of sample neutralized 10 mL of 1 M H_2SO_4. The percentage of nitrogen in the soil is

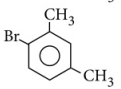
(a) 37.33 (b) 45.33

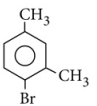
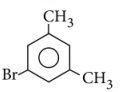
(c) 35.33 (d) 43.33

39. What products are formed when the following compound is treated with Br_2 in the presence of $FeBr_3$?

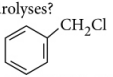
(a) 

(b)  and 

(c)  and 

(d)  and 

40. Which of the following compounds will undergo racemisation when solution of KOH hydrolyses?

(i) 

(ii) $CH_3CH_2CH_2Cl$

(iii) $H_3C-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2Cl$

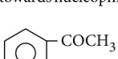
(iv) 

(a) (i) and (ii) (b) (ii) and (iv)
(c) (iii) and (iv) (d) (i) and (iv)

41. Among the following sets of reactants which one produces anisole?
(a) CH_3CHO ; *R*Mg*X*
(b) C_6H_5OH ; NaOH ; CH_3I
(c) C_6H_5OH ; neutral $FeCl_3$
(d) $C_6H_5CH_3$; CH_3COCl ; $AlCl_3$

42. Which of the following will not be soluble in sodium hydrogen carbonate?
(a) 2,4,6-Trinitrophenol
(b) Benzoic acid
(c) *o*-Nitrophenol
(d) Benzenesulphonic acid

43. Which one is most reactive towards nucleophilic addition reaction?

(a)  (b) 

(c)  (d) 

44. Identify *Z* in the sequence of reactions :

$$CH_3CH_2CH=CH_2 \xrightarrow{HBr/H_2O_2} Y \xrightarrow{C_2H_5ONa} Z$$

(a) $CH_3-(CH_2)_3-O-CH_2CH_3$
(b) $(CH_3)_2CH-O-CH_2CH_3$
(c) $CH_3(CH_2)_4-O-CH_3$
(d) $CH_3CH_2-CH(CH_3)-O-CH_2CH_3$

45. Which of the following organic compounds has same hybridization as its combustion product (CO_2)?
(a) Ethane (b) Ethyne
(c) Ethene (d) Ethanol

SOLUTIONS

1. (a) : Only one orbital, $3p_z$ has following set of quantum numbers, $n = 3$, $l = 1$ and $m_l = 0$.

2. (d) : $E = \frac{hc}{\lambda}$ [Given, $\lambda = 45\text{ nm} = 45 \times 10^{-9}$ m]

On putting the given values in the equation, we get

$$E = \frac{6.63\times10^{-34}\times3\times10^{8}}{45\times10^{-9}} = 4.42\times10^{-18}\text{ J}$$

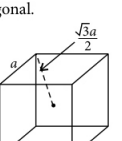
3. (c): According to Avogadro's hypothesis, ratio of the volumes of gases will be equal to the ratio of their no. of moles.

So, no. of moles $= \frac{\text{Mass}}{\text{Mol. mass}}$

$n_{H_2} = \frac{w}{2}$; $n_{O_2} = \frac{w}{32}$; $n_{CH_4} = \frac{w}{16}$

So, the ratio is $\frac{w}{2} : \frac{w}{32} : \frac{w}{16}$ or $16:1:2$.

4. (d) : The distance between the body centered atom and one corner atom is $\frac{\sqrt{3}a}{2}$ *i.e.* half of the body diagonal.



5. (d) : Tyndall effect is due to the scattering of light by colloidal particles and not due to the charge.

6. (c): Na_2CO_3 which is a salt of NaOH (strong base) and H_2CO_3 (weak acid) will produce a basic solution with pH greater than 7.

7. (c): $\Delta T_f = i \times K_f \times m$

So, $\Delta T_f \propto i$ (van't Hoff factor)

Salt	*i*
KCl	2
$C_6H_{12}O_6$	1
$Al_2(SO_4)_3$	5
K_2SO_4	3

Hence, *i* is maximum *i.e.*, 5 for $Al_2(SO_4)_3$.

8. (a) : 1 mole ≡ 22.4 litres at S.T.P.

$$n_{H_2} = \frac{22.4}{22.4} = 1 \text{ mol}$$

$$n_{Cl_2} = \frac{11.2}{22.4} = 0.5 \text{ mol}$$

Reaction is as,

$$H_{2(g)} + Cl_{2(g)} \longrightarrow 2HCl_{(g)}$$

Initial	1 mol	0.5 mol	0
Final	(1 – 0.5) = 0.5 mol	(0.5 – 0.5) = 0 mol	2 × 0.5 = 1 mol

Here, Cl_2 is limiting reagent. So, 1 mole of $HCl_{(g)}$ is formed.

9. (c): The oxidation reaction is

$$\underset{0.1 \text{ mol}}{\overset{+6}{MnO_4^{2-}}} \longrightarrow \underset{0.1 \text{ mol}}{\overset{+7}{MnO_4^-}} + e^-$$

$Q = 0.1 \times F = 0.1 \times 96500 \text{ C} = 9650 \text{ C}$

10. (b) : $\Delta G^\circ = -2.303RT \log K_{sp}$

$63.3 \times 10^3 \text{ J} = -2.303 \times 8.314 \times 298 \log K_{sp}$

$63.3 \times 10^3 \text{ J} = -5705.84 \log K_{sp}$

$$\log K_{sp} = -\frac{63.3 \times 10^3}{5705.84} = -11.09$$

$K_{sp} = \text{antilog}(-11.09) = 8.128 \times 10^{-12}$

11. (d) : According to Faraday's second law,

$$\frac{W_{Ag}}{E_{Ag}} = \frac{W_{O_2}}{E_{O_2}} \quad \text{or} \quad \frac{W_{Ag}}{108} = \frac{5600}{22400} \times \frac{32}{8}$$

$$\text{or } \frac{W_{Ag}}{108} = \frac{8}{8} \quad \Rightarrow \quad W_{Ag} = 108 \text{ g}$$

12. (b) : Using Gibb's-Helmholtz equation,

$\Delta G = \Delta H - T\Delta S$

During adsorption of a gas, entropy decreases *i.e.* $\Delta S < 0$

For spontaneous adsorption, ΔG should be negative, which is possible when ΔH is highly negative.

13. (d) : As the forward reaction is exothermic and leads to lowering of pressure (produces lesser number of gaseous moles) hence, according to Le Chatelier's principle, at high pressure and low temperature, the given reversible reaction will shift in forward direction to form more product.

14. (b) : $\Delta H = \Delta U + \Delta n_g RT$

Given, $\Delta U = 2.1$ kcal, $\Delta n_g = 2$,

$R = 2 \times 10^{-3}$ kcal, $T = 300$ K

$\therefore \quad \Delta H = 2.1 + 2 \times 2 \times 10^{-3} \times 300 = 3.3$ kcal

Again, $\Delta G = \Delta H - T\Delta S$

Given, $\Delta S = 20 \times 10^{-3}$ kcal K^{-1}

On putting the value of ΔH in the equation, we get

$\Delta G = 3.3 - 300 \times 20 \times 10^{-3}$

$= 3.3 - 6 \times 10^3 \times 10^{-3} = -2.7$ kcal

15. (a) : $\log \frac{K'_p}{K_p} = -\frac{\Delta H}{2.303R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$

For exothermic reaction, ΔH = –ve *i.e.* heat is evolved. The temperature T_2 is higher than T_1.

Thus, $\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$ is negative.

so, $\log K'_p - \log K_p$ = –ve or $\log K_p > \log K'_p$

or $K_p > K'_p$

16. (none) : Cations lose electrons and are smaller in size than the parent atom, whereas anions add electrons and are larger in size than the parent atom. Hence, the order is $H^- > H > H^+$.

For isoelectronic species, the ionic radii decreases with increase in atomic number *i.e.* nuclear charge.

Hence, the correct orders are

$O^{2-} > F^- > Na^+$ and $N^{3-} > Mg^{2+} > Al^{3+}$.

17. (a) : $n_{Mg} = \frac{1}{24} = 0.0416$ moles

$$n_{O_2} = \frac{0.56}{32} = 0.0175 \text{ moles}$$

The balanced equation is

$$Mg + \frac{1}{2}O_2 \longrightarrow MgO$$

Initial	0.0416 moles	0.0175 moles	0
Final	$(0.0416 - 2 \times 0.0175)$	0	2×0.0175
	$= 0.0066$ moles (O_2 is limiting reagent)		

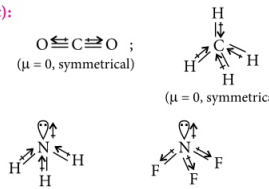
$\therefore$ Mass of Mg left in excess $= 0.0066 \times 24 = 0.16$ g

18. (c): Both $FeCl_2$ and $SnCl_2$ are reducing agents with low oxidation numbers.

19. (b) :

Species	No. of electrons
Be^{2+}	2
H^+	1
Li^+	2
Na^+	10
Mg^{2+}	10

20. (c):

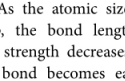


($\mu = 0$, symmetrical) ; ($\mu = 0$, symmetrical)

($\mu \neq 0$, pyramidal) ($\mu \neq 0$, pyramidal)

In NH_3, H is less electronegative than N and hence dipole moment of each N—H bond is towards N and create high net dipole moment whereas in NF_3, F is more electronegative than N, the dipole moment of each N—F bond is opposite to that of lone pair, hence reducing the net dipole moment.

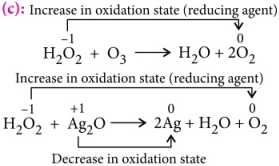
21. (b) :



(sp^2-hybridised, trigonal planar)

22. (a) : As the atomic size increases down the group, the bond length increases and the bond strength decreases and the cleavage of *E*–H bond becomes easier thus, more will be the acidity. Thus, the correct order is : $H_2S < H_2Se < H_2Te$.

23. (c): Increase in oxidation state (reducing agent)



Decrease in oxidation state

H_2O_2 acts as reducing agent in all those reactions in which O_2 is evolved.

24. (c): Aspartame is stable under cold conditions but unstable at cooking temperature.

25. (c): CrO_5 has butterfly structure having two peroxo bonds.

Peroxo oxygen has –1 oxidation state.
Let oxidation state of Cr be '*x*'
$CrO_5 : x + 4(-1) + 1(-2) = 0 \Rightarrow x = +6$

26. (b) : Hydrogen peroxide is oxidised to H_2O and O_2.

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

or, $$2MnO_4^- + 5H_2O_2 + 6H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2$$

27. (b) : H_2O is a weak field ligand, hence $\Delta_o <$ pairing energy.
$CFSE = (-0.4x + 0.6y)\Delta_o$
where, x and y are no. of electrons occupying t_{2g} and e_g orbitals respectively.
For $[Fe(H_2O)_6]^{3+}$ complex ion,
$Fe^{3+}(3d^5) = t_{2g}^3 e_g^2$
$= -0.4 \times 3 + 0.6 \times 2 = 0.0$ or 0 Dq

28. (b) : Magnetic moment is given by

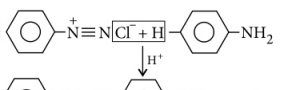
$\mu = \sqrt{n(n+2)}$ B.M.

[where n = no. of unpaired electrons]
When $n = 2$, then $\mu = 2.83$ B.M.
For $Ti^{3+}(3d^1)$, $n = 1$; $Cr^{3+}(3d^3)$, $n = 3$
$Ni^{2+}(3d^8)$, $n = 2$; $Mn^{2+}(3d^5)$, $n = 5$
Hence, Ni^{2+} has two unpaired electrons, with magnetic moment 2.83 B.M.

29. (b)

30. (a) : Due to poor shielding effect of 4*f*-orbitals, nucleus will exert a strong attraction and size of atom or ion goes on decreasing as move in the series with increase in atomic number.

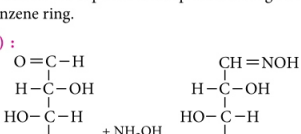
31. (d) :



p-Aminoazobenzene (yellow dye)
(*A*)

32. (b) : Aromatic diazonium salts are more stable due to dispersal of the positive charge in benzene ring.

33. (d) :

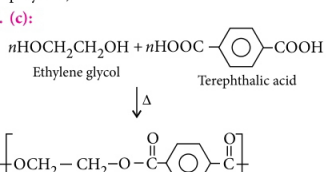


D(+)-Glucose Glucoxime

34. (c): Adrenaline hormone helps to release fatty acids from fat and glucose from liver glycogen under the condition of stress. Hence, it is also called 'flight or fight hormone'.

35. (d) : (a) - Neoprene rubber (elastomer)
(b) - PVC (thermoplastic polymer)
(c) - Nylon-6,6 (fibre)
(d) - Novolac which further undergoes cross linking to produce bakelite (thermosetting polymer).

36. (c):



Ethylene glycol Terephthalic acid

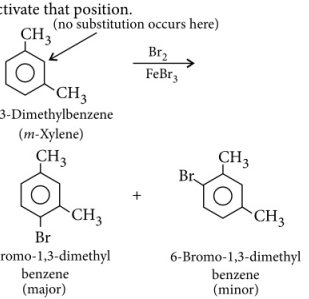
Terylene (Dacron)

37. (d)

38. (a) : $H_2SO_4 + 2NH_3 \longrightarrow (NH_4)_2SO_4$
10 mL of 1 M H_2SO_4 = 10 mmol
[... $M \times V_{(mL)}$ = mmol]
NH_3 consumed = 20 mmol
Acid used for the absorption of ammonia
= 20 – 10 mmol
= 10 mL of 2 N (or 1 M) H_2SO_4

$$\% \text{ of N} = \frac{1.4 \times N \times V}{W} = \frac{1.4 \times 2 \times 10}{0.75} = 37.33\%$$

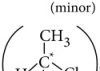
39. (c): $-CH_3$ group is *o*,*p*-directing. Because of crowding, no substitution occurs at the carbon atom between the two $-CH_3$ groups in *m*-Xylene, even though two $-CH_3$ groups activate that position.

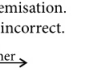


1,3-Dimethylbenzene (*m*-Xylene)

4-Bromo-1,3-dimethyl benzene (major)

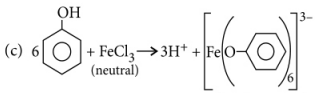
6-Bromo-1,3-dimethyl benzene (minor)

40. (none) : Due to chirality  , only compound (d) will undergo racemisation. Hence, all the given options are incorrect.

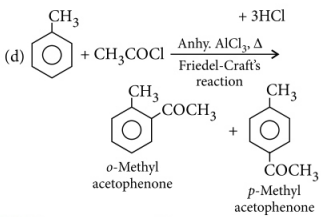
41. (b) : (a) $CH_3CHO + RMgX \xrightarrow{\text{ether}}$ 
2° alcohol

(b) $C_6H_5OH + NaOH \xrightarrow[-H_2O]{} C_6H_5ONa$ Sodium phenoxide

$C_6H_5OCH_3 + NaI \xleftarrow[\Delta]{CH_3I}$
Methyl phenyl ether (Anisole) (Williamson's synthesis)

(c) 

Violet colour complex

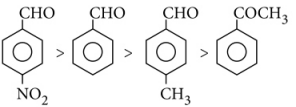
(d) 

42. (c): The reaction is as follows:

$$\text{Acid} + NaHCO_3 \longrightarrow \underset{\text{(soluble)}}{\text{Sodium salt of acid}} + H_2CO_3$$

Among all the given compounds, *o*-nitrophenol is weaker acid than HCO_3^-. Hence, it does not react with $NaHCO_3$.

43. (d) : Aromatic aldehydes are more reactive than alkyl aryl ketones. Electron withdrawing group ($-NO_2$) increases the reactivity towards nucleophilic addition reactions whereas, electron donating group ($-CH_3$) decreases the reactivity towards nucleophilic addition reactions. Therefore, the order is :



44. (a) : $CH_3CH_2CH{=}CH_2 \xrightarrow[\text{(peroxide or anti-markovnikov's effect)}]{HBr/H_2O_2} CH_3CH_2\underset{\underset{H}{|}}{CH}-\underset{\underset{Br}{|}}{CH_2}$ (1-Bromobutane, *Y*)

$CH_3CH_2CH_2CH_2-O-CH_2CH_3$ (*Z*)

45. (b) : $C_2H_2 + \frac{5}{2}O_2 \longrightarrow 2CO_2 + H_2O$

Both ethyne and CO_2 have *sp*-hybridisation.

$\overset{sp}{O}=\overset{sp}{C}=O \qquad \overset{sp}{H}C\equiv\overset{sp}{C}H$

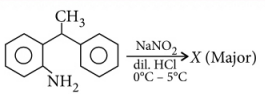
CONCEPT BOOSTER

Dear students!! This month I have included another important chapter 'organic compounds containing nitrogen'. In various competitive examinations, lots of tricky and conceptual questions are asked from this chapter. Please practice the questions given in this article. Stay well, good luck!!!!!

*Arunava Sarkar

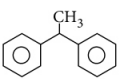
ORGANIC COMPOUNDS CONTAINING NITROGEN

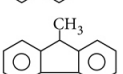
SINGLE CORRECT ANSWER TYPE

1. 

Identify *X*.

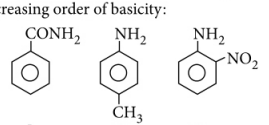
(a) 

(b) 

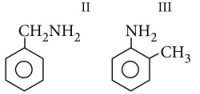
(c) 

(d) None of these.

2. Arrange the followings according to the increasing order of basicity:



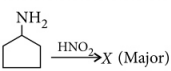
I II III



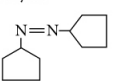
IV V

(a) II < III < IV < I < V (b) I < III < V < II < IV

(c) III < II < I < V < IV (d) I < II < III < V < IV

3. 

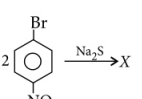
Identify *X*.

(a) 

(b) 

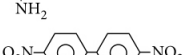
(c) 

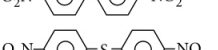
(d) None of these.

4. 

Identify *X*.

(a) 

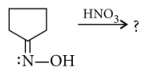
(b) 

(c) 

(d) None of these.

* Institute of Chemistry (IOC)- Asansol, Durgapur, Dhanbad, Burdwan, Kolkata, Jamshedpur, Bokaro, Patna 09732313208

5. Identify the major product in the following reaction:

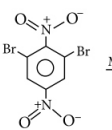


(a) 

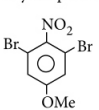
(b) 

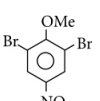
(c) 

(d) 

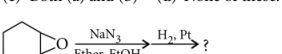
6. 

Identify the product.

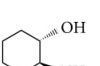
(a) 

(b) 

(c) Both (a) and (b) (d) None of these.

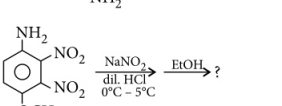
7. 

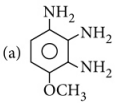
(a) 

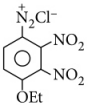
(b) 

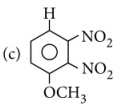
(c) 

(d) None of these.

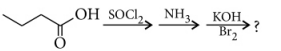
8. 

(a) 

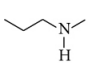
(b) 

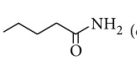
(c) 

(d) None of these.

9. 

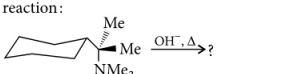
(a) 

(b) 

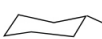
(c) 

(d) None of these.

10. Identify the major product in the following reaction:

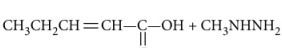


(a) 

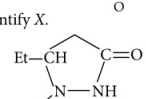
(b) 

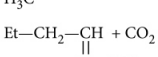
(c) 

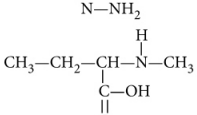
(d) None of these.

11. 

Identify *X*.

(a) 

(b) 

(c) 

(d) None of these.

CONCEPT MAP — ORGANIC COMPOUNDS CONTAINING NITROGEN

Amines

$R-NH_2$

Common name : Alkylamines
IUPAC name : Alkanamines

sp^3-C: $R \perp \ddot{N}$ — Alkyl amine
sp^2-C: $Ar \perp \ddot{N}$ — Aromatic amine

Classified as : $R-NH_2$(1°); R_2NH(2°); R_3N(3°)

$R_4N^+X^-$ (4°- ammonium salt)

Preparation

- $R-COOH + N_3H \xrightarrow[\text{Schmidt reaction}]{\text{Conc. } H_2SO_4}$
- $R-CN \xrightarrow[\text{Mendius reaction}]{H_2/Ni;\ Na/C_2H_5OH}$
- $R-NO_2 \xrightarrow{Sn/HCl;\ LiAlH_4}$
- Gabrial phthalimide synthesis: $\xrightarrow[H_2O,\ HCl,\ \Delta]{+\ KOH;\ C_6H_5X}$

$\rightarrow R-NH_2$

Chemical Properties

- $\xrightarrow[\text{Carbylamine reaction}]{CHCl_3 + 3KOH,\ \Delta}$ RNC (Alkyl isocyanide)
- $\xrightarrow[\Delta]{R-CHO}$ $RN=CHR'$ (Schiff's base (Aldimine))

Basic Nature

- Aliphatic amine > NH_3 > aromatic amine
- 3° > 2° > 1° > NH_3 [in gas phase or in non aq. solvent]
- 2° > 1° > 3° > NH_3 [in aq. phase, only $-CH_3$ subs. amine]
- 2° > 3° > 1° > NH_3 [in aq. phase, only $-C_2H_5$ subs. amine]

Special Hofmann Reactions

- **Hofmann's method (Separation of 1°, 2° and 3° amines):**
  Diethyloxalate + 1°+ 2°+ 3° amines
  - Oxamide, solid (1° amine)
  - Oxamic ester, liquid (2° amine)
  - No reaction (3° amine)
- **Hofmann's ammonolysis (Mix. of amines is formed):** $RX + NH_3 \longrightarrow \underbrace{1° + 2° + 3° + 4°}_{\text{Amines}}$
- **Hofmann's bromamide/degradation (Only 1° amine is formed):**
  $R-CONH_2 + Br_2 + 4KOH \xrightarrow{\Delta}$
  $R-NH_2 + 2KBr + K_2CO_3 + 2H_2O$
- **Hofmann's mustard oil reaction (Test for only 1° amine)**
  $R-NH_2 + CS_2 + HgCl_2 \xrightarrow{\Delta}$
  $R-N=C=S + HgS + 2HCl$
  Alkyl isothiocyanate

Distinction Tests

- **Liebermann's nitroso test:**
  HONO + 1°+ 2°+ 3° amines
  - $R-OH + N_2\uparrow + H_2O$ [For 1° amine] (*Exception* - CH_3NH_2 *form methyl nitrite or dimethyl ether*)
  - $R_2NNO + H_2O$ [For 2° amine] (*N*-Nitrosodialkylamine (yellow oily liquid)
  - $[R_3NH]^+NO_2^- \xrightarrow{\Delta} R-OH + R_2NN=O$ [For 3° amine] (Nitrite salt; Nitrosoamine)
- **Hinsberg's test:**
  $C_6H_5SO_2Cl$ + 1°+ 2°+ 3° amines
  - Clear solution $\xrightarrow{KOH}$ Soluble salt [For 1° amine]
  - PPt. $\xrightarrow{KOH}$ No reaction [For 2° amine]
  - No reaction [For 3° amine]

Cyanides

$R-C\equiv N$

Common name : Alkyl cyanides
IUPAC name : Alkane nitriles

Preparation

- $RX + KCN \xrightarrow[\Delta]{100\ °C}$
- $R-CONH_2 \xrightarrow[\Delta]{P_2O_5}$
- $R-NH_2 \xrightarrow[500\ °C]{Cu/Ni}$

$\rightarrow RCN$

Chemical Properties

RCN:
- $\xrightarrow[SnCl_2/HCl]{+2[H]}$ R CHO (Stephen's reaction)
- $\xrightarrow{RMgX}$ $RCOR'$
- $\xrightarrow[\text{alk. } H_2O_2]{H_2O}$ RCOOH

Isocyanides

$R-N\overset{+}{\equiv}\overset{-}{C}$

Common name : Alkyl isocyanides
IUPAC name : Alkyl carbylamines

Preparation

- $RX + AgCN \xrightarrow[\Delta]{C_2H_5OH}$
- $RCONHR \xrightarrow[\text{Pyridine}]{POCl_3}$

$\rightarrow RNC$

Chemical Properties

RNC:
- $\xrightarrow{H_2O/H^+}$ RNH_2
- $\xrightarrow{+4[H]}$ $RNHCH_3$
- $\xrightarrow[250°C]{Na/C_2H_5OH,\ \Delta}$ RCN

Nitro

$R-N\overset{O}{\overset{O}{}}$

IUPAC name : Nitroalkanes

Preparation

- $R-X + AgNO_2 \xrightarrow{\Delta}$
- $R(Cl)COOH \xrightarrow[-NaCl/\Delta]{NaNO_2}$

$\rightarrow R-NO_2$

Chemical Properties

$\xrightarrow{\Delta}$
- explosion: $1/2N_2 + CO_2 + 3/2H_2$
- $\xrightarrow[Sn/HCl\ (acidic)]{+6[H]}$ RNH_2
- $\xrightarrow[Zn + NH_4Cl\ (neutral)]{+4[H]}$ $R-NHOH$
- $\xrightarrow{Aq.\ TiCl_3}$ $R-CHO$

Aromatic Compounds

Diazonium Salt

$C_6H_5N_2^+Cl^-$

- $\xrightarrow[\Delta]{CuCl/HCl}$ C_6H_5Cl [Sandmeyer reaction]
- $\xrightarrow{Cu/HCl}$ C_6H_5Cl [Gattermann reaction]
- $\xrightarrow[NaOH,\ \Delta]{C_6H_6}$ $C_6H_5-C_6H_5$ [Gomberg reaction]
- $\xrightarrow{Phenol}$ $C_6H_5N=NC_6H_4OH$ [Coupling reaction]
- $\xrightarrow{H_2O/H^+}$ C_6H_5OH
- $\xrightarrow{HBF_4/\Delta}$ C_6H_5F

Aniline

Preparation

- $C_6H_6 + Cl-NH_2 \xrightarrow[\Delta]{Anhy.\ AlCl_3}$
- $C_6H_5COOH + N_3H \xrightarrow[\text{Schmidt reaction}]{\text{Conc. } H_2SO_4}$
- $C_6H_5OH + NH_3 \xrightarrow[300\ °C]{Anhy.\ ZnCl_2}$

$\rightarrow C_6H_5NH_2$

Chemical Properties

$C_6H_5NH_2$:
- $\xrightarrow{HCl/0\text{-}5\ °C}$ $C_6H_5NH_3^+Cl^-$
- $\xrightarrow{[O]/acidified\ KMnO_4}$ Aniline black
- $\xrightarrow{[O]/alkaline\ KMnO_4}$ Azobenzene
- $\xrightarrow{[O]/neutral\ KMnO_4}$ Azobenzene and nitrobenzene

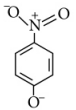
Nitrobenzene

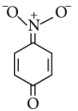
$C_6H_5NO_2$

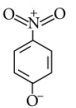
- $\xrightarrow{2[H]}$ C_6H_5NO (Nitrosobenzene) $\xrightarrow{2[H]}$ C_6H_5NHOH (Phenylhydroxyl amine) $\xrightarrow[Sn + HCl]{acidic}$ $C_6H_5NH_2$ (Aniline)
- $\xrightarrow[\text{Isomeric change}]{}$ $H_2NC_6H_4OH$ (*p*-Amino phenol)
- $\xrightarrow[NaOH]{Na_3AsO_3}$ in alkaline medium

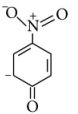
$C_6H_5N \rightarrow O$ (Azoxybenzene) $\xrightarrow{Zn + NaOH}$ C_6H_5N (Azobenzene) $\xrightarrow{Zn + NaOH}$ C_6H_5NH (Hydrazobenzene)

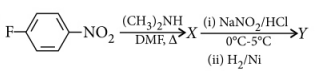
12. The most unlikely representation of resonance structures of *p*-nitrophenoxide ion is

(a) 

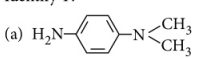
(b) 

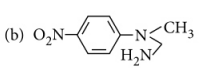
(c) 

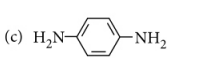
(d) 

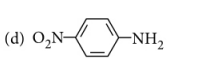
13. 

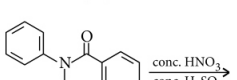
Identify *Y*.

(a) 

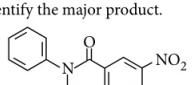
(b) 

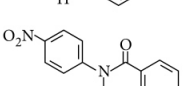
(c) 

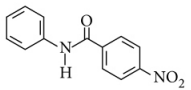
(d) 

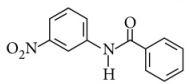
14. 

Identify the major product.

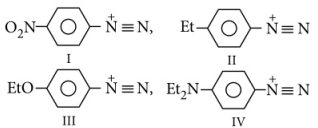
(a) 

(b) 

(c) 

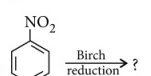
(d) 

15. Arrange the following diazonium ions according to the increasing order of reactivity in diazo coupling reaction with phenol in the presence of dilute alkali.



(a) I > II > III > IV (b) II > I > III > IV

(c) III > IV > II > I (d) None of these.

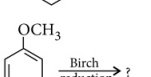
16. 

(a) 

(b) 

(c) 

(d) None of these.

17. 

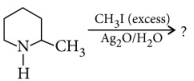
(a) 

(b) 

(c) 

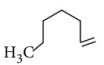
(d) None of these.

18. Identify the major product in the following reaction:



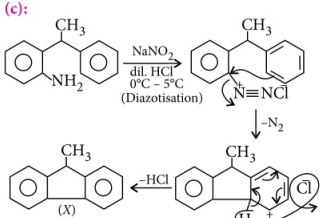
(a) 

(b) $CH_2{=}CH(CH_2)_2CH{=}CH_2$

(c)  (d) None of these.

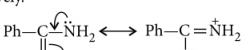
SOLUTIONS

1. (c):



So, correct option is (c).

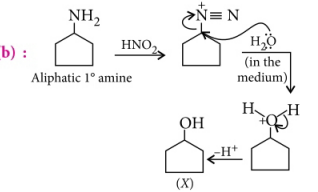
2. (b) : Amides are very weak bases. Lone pair above nitrogen atom takes part in resonance actively.



This is why I is least basic.

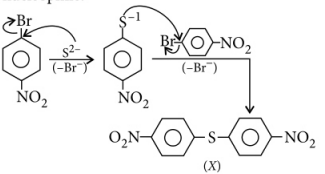
IV is the strongest base as here lone pair above nitrogen atom does not take part in resonance because the nitrogen atom is not attached directly with the benzene ring. Due to ortho effect, V and III are less basic than II. Among III and V, V is more basic than III because $-CH_3$ group has $+I$ effect and hyperconjugation effect. So, option (b) is correct.

3. (b) :



Remember that aliphatic 1° amine, in diazotisation type reaction converts into 1° alcohol.

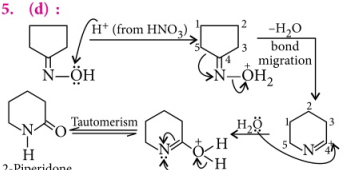
4. (c): It is nucleophilic aromatic substitution reaction ($S_{Ar}N$). Here, S^{2-} from Na_2S is the nucleophile.



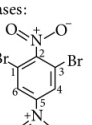
$-NO_2$ at the *para* position enhances the rate of nucleophilic aromatic substitution reaction.

So, correct option is (c).

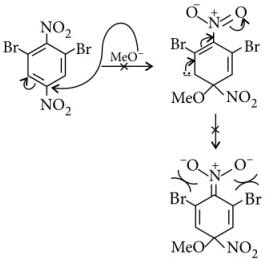
5. (d) :



6. (b) : This question is based on SIR (steric inhibition resonance) effect, there are two possible cases:

Case I : 

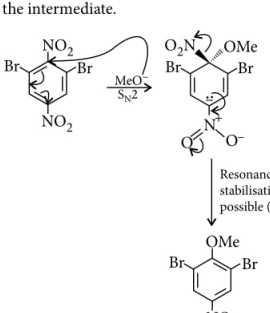
attack by MeO^- at C-5 will generate the following structure:



Here, for the participation of $-NO_2$ in the resonance, *p*-orbital of nitrogen atom must be parallel with the *p*-orbital of the carbon atom which is bearing the $-NO_2$ group and for this the oxygen atoms of $-NO_2$ group must be coplanar with the benzene ring but here it is not possible as the —Br atoms create SIR.

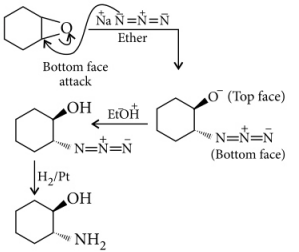
So, reaction is not possible here.

Case II : However, if the attack takes place at C-2, then $-NO_2$ group attached with C-5 can easily participate in the resonance to stabilise the intermediate.



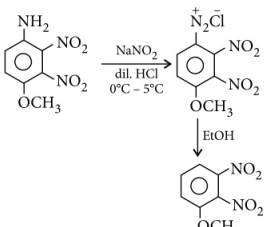
So, correct option is (b).

7. (c):



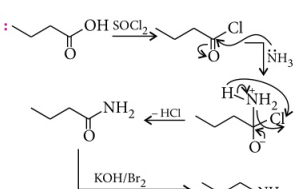
So, option (c) is correct.

8. (c):



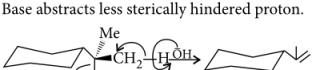
So, option (c) is correct.

9. (a) :



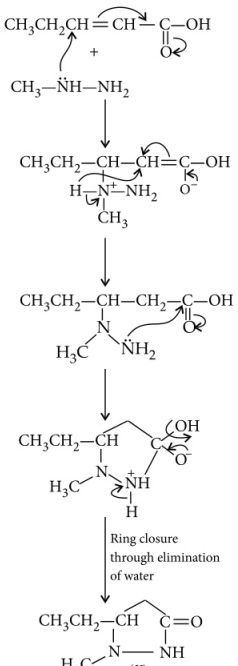
So, correct option is (a).

10. (c): It is a clear Hofmann's elimination reaction. Base abstracts less sterically hindered proton.

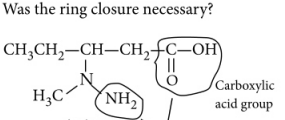


So, option (c) is correct.

11. (a) :

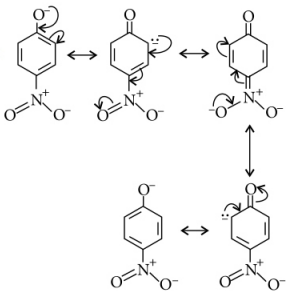


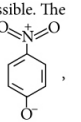
Was the ring closure necessary?



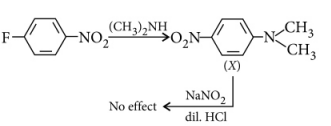
Reaction is possible because one group is carboxylic acid and the another group is amine. So, acidic and basic groups will definitely react at least at that time when the ring will be of five or six membered.

12. (c):

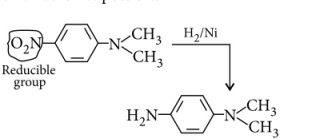


Therefore, the structure (c) is not possible. The logic is also that in the structure  , nitrogen atom has five bonds and also contains a positive charge which is impossible.

13. (a) : $(CH_3)_2NH$ is a good base. It can substitute fluorine through benzyne mechanism. Presence of $-NO_2$ group even promotes it.

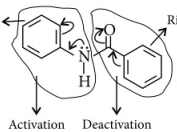


As there is no hydrogen atom bonded with the nitrogen atom formation of benzene diazonium chloride is not possible.



So, correct option is (a).

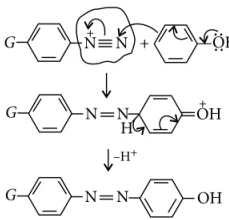
14. (b) :



This is very important to notice that what type of group is attached with the rings. Nitrogen through its $+R$ effect activates ring 1 whereas $-\overset{\overset{O}{\|}}{C}-$group deactivates ring 2. Naturally, $-\overset{+}{N}O_2$ (the electrophile coming from HNO_3 and H_2SO_4) will enter into ring 1 it will enter at the *para* position predominantly as there will be steric problem at the *ortho* position. So, correct answer is (b).

15. (a) :

Mechanism:

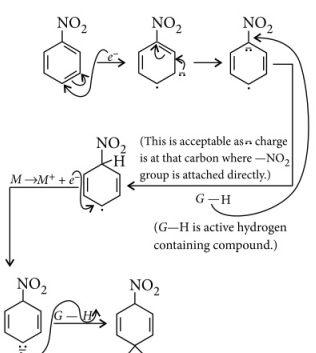


In the initial step of diazo coupling reaction π electrons pair between the triple bonded nitrogen atoms opens towards the positively charged nitrogen atom. Faster this opening will be, faster will be the rate of the reaction. Reaction rate and success of the reaction will be enhanced if —*G* is an EWG which makes positively charged nitrogen atom even more electron deficient.

$-NO_2$ group is purely and highly electron withdrawing. All the other groups *i.e.* —Et, $-Et_2N$, —EtÖ are electron donating and their electron donating ability order is $-Et_2N$ > —EtO > —Et. So, the rate of the given diazonium salts in diazo coupling reaction will be I > II > III > IV.

So, the correct option is (a).

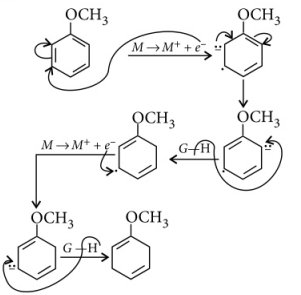
16. (a) : M (Metal) $\longrightarrow M^+ + e^-$



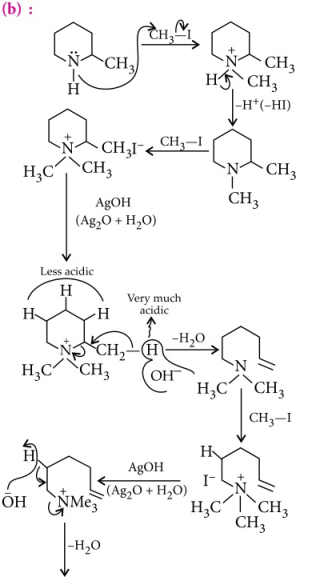
So, correct option is (a).

[Note : EWGs will fetch eventually  this skeleton.]

17. (a) :



18. (b) :



SOLVED PAPER 2014

Kerala PET

1. A 250 W electric bulb of 80% efficiency emits a light of 6626 Å wavelength. The number of photons emitted per second by the lamp is ($h = 6.626 \times 10^{-34}$ Js)
(a) 1.42×10^{17} (b) 2.18×10^{16}
(c) 6.66×10^{20} (d) 2.83×10^{16}
(e) 4.25×10^{16}

2. The shortest wavelength of the line in hydrogen atomic spectrum of Lyman series when $R_H = 109678\ cm^{-1}$ is
(a) 1002.7 Å (b) 1215.67 Å
(c) 1127.30 Å (d) 911.7 Å
(e) 1234.7 Å

3. The work function of a metal is 5 eV. What is the kinetic energy of the photoelectron ejected from the metal surface if the energy of the incident radiation is 6.2 eV? ($1\ eV = 1.6 \times 10^{-19}$ J)
(a) 6.626×10^{-19} J (b) 8.01×10^{-19} J
(c) 1.92×10^{-18} J (d) 8.010×10^{-18} J
(e) 1.92×10^{-19} J

4. The lattice energy of NaCl is 788 kJ mol^{-1}. This means that 788 kJ of energy is required
(a) to separate one mole of solid NaCl into one mole of $Na_{(g)}$ and one mole of $Cl_{(g)}$ to infinite distance
(b) to separate one mole of solid NaCl into one mole of $Na^+_{(g)}$ and one mole of $Cl^-_{(g)}$ to infinite distance
(c) to convert one mole of solid NaCl into one mole of gaseous NaCl
(d) to convert one mole of gaseous NaCl into one mole of solid NaCl
(e) to separate one mole of gaseous NaCl into one mole of $Na^+_{(g)}$ and one mole of $Cl^-_{(g)}$ to infinite distance.

5. Arrange the following species in the correct order of their stability : C_2, Li_2, O_2^+, He_2^+
(a) $Li_2 < He_2^+ < O_2^+ < C_2$
(b) $C_2 < O_2^+ < Li_2 < He_2^+$
(c) $He_2^+ < Li_2 < C_2 < O_2^+$
(d) $O_2^+ < C_2 < Li_2 < He_2^+$
(e) $C_2 < Li_2 < He_2^+ < O_2^+$

6. Molecular formulae and shapes of some molecules are given below. Choose the incorrect match.

	Formula		Shape
(a)	NH_3	—	Trigonal pyramidal
(b)	SF_4	—	Tetrahedral
(c)	ClF_3	—	T-shaped
(d)	PCl_5	—	Trigonal bipyramidal
(e)	BF_3	—	Trigonal planar

7. Potassium dichromate belongs to which crystal system?
(a) Tetragonal (b) Orthorhombic
(c) Triclinic (d) Hexagonal
(e) Monoclinic

8. If two moles of an ideal gas at 500 K occupies a volume of 41 litres, the pressure of the gas is ($R = 0.082$ L atm K^{-1} mol^{-1})
(a) 2 atm (b) 3 atm
(c) 4 atm (d) 5 atm
(e) 1 atm

9. At 273 K, the density of a certain gaseous oxide at 2 atmosphere is same as that of dioxygen at 5 atmosphere. The molecular mass of the oxide (in g mol^{-1}) is
(a) 80 (b) 64
(c) 32 (d) 160
(e) 70

10. The reaction of H_2 is given below :

$$H_2 + CO + R - CH = CH_2 \longrightarrow R - CH_2 - CH_2 - CHO$$

is specifically called as

(a) hydrogenation (b) reduction
(c) hydroformylation (d) dehydration
(e) formylation

11. Which of the following are isoelectronic species?

(i) NH_3 (ii) CH_3^+
(iii) NH_2^- (iv) NH_4^+

Choose the correct answer from the codes given below :

(a) (i), (ii), (iii) (b) (ii), (iii), (iv)
(c) (i), (ii), (iv) (d) (i), (iii), (iv)
(e) (ii), (iii)

12. The salt of an alkali metal gives violet colour in the flame test. Its aqueous solution gives a white precipitate with barium chloride in hydrochloric acid medium. The salt is

(a) K_2SO_4 (b) KCl
(c) Na_2SO_4 (d) K_2CO_3
(e) Li_2SO_4

13. In which one of the following the central atom is sp^3 hybridized?

(a) NH_4^+ (b) BF_3
(c) SF_6 (d) PCl_5
(e) XeF_4

14. Which one of the following statements is not true in respect of properties of interhalogen compounds?

(a) They are all covalent compounds.
(b) They are volatile solids or liquids except ClF.
(c) IF_5 has square pyramidal structure.
(d) They are all paramagnetic in nature.
(e) BrF_3 is used in the preparation of UF_6 in the enrichment of ^{235}U.

15. Which one of the following is an incorrect statement?

(a) O_3 oxidises PbS to $PbSO_4$.
(b) O_3 oxidises nitric oxide to nitrogen dioxide.
(c) O_3 oxidises aqueous KI at pH = 9.2.
(d) The two oxygen-oxygen bond lengths in O_3 are different.
(e) O_3 is used as an oxidizing agent in the manufacture of $KMnO_4$.

16. The correct descending order of oxidizing power of the following is

(a) $Cr_2O_7^{2-} > MnO_4^- > VO_2^+$
(b) $MnO_4^- > Cr_2O_7^{2-} > VO_2^+$
(c) $VO_2^+ > MnO_4^- > Cr_2O_7^{2-}$
(d) $MnO_4^- > VO_2^+ > Cr_2O_7^{2-}$
(e) $Cr_2O_7^{2-} > VO_2^+ > MnO_4^-$

17. The number of electrons that are involved in the reduction of permanganate to manganese(II) salt, manganate and manganese dioxide respectively are

(a) 5, 1, 3 (b) 5, 3, 1
(c) 2, 7, 1 (d) 5, 2, 3
(e) 2, 3, 1

18. The calculated magnetic moment of a divalent ion of an atom with atomic number 24 in aqueous solution is

(a) 4.90 BM (b) 5.92 BM
(c) 3.87 BM (d) 2.84 BM
(e) 1.73 BM

19. The entropy of vaporization of a liquid is 58 J K^{-1} mol^{-1}. If 100 g of its vapour condenses at its boiling point of 123 °C, the value of entropy change for the process is
(Molar mass of the liquid = 58 g mol^{-1})

(a) −100 J K^{-1} (b) 100 J K^{-1}
(c) −123 J K^{-1} (d) 123 J K^{-1}
(e) 1230 J K^{-1}

20. The values of limiting ionic conductance of H^+ and $HCOO^-$ ions are respectively 347 and 53 S cm^2 mol^{-1} at 298 K. If the molar conductance of 0.025 M methanoic acid at 298 K is 40 S cm^2 mol^{-1}, the dissociation constant of methanoic acid at 298 K is

(a) 1×10^{-5} (b) 2×10^{-5}
(c) 1.5×10^{-4} (d) 2.5×10^{-5}
(e) 2.5×10^{-4}

21. In a closed cylinder of capacity 24.6 L the following reaction occurs at 27 °C, $A_{2(s)} \rightleftharpoons B_{2(s)} + 2C_{(g)}$. At equilibrium 1 g of

$B_{2(s)}$ (molar mass = 50 g mol^{-1}) is present. The equilibrium constant K_p for the equilibrium in atm^2 unit is
(R = 0.082 L atm K^{-1} mol^{-1})
(a) 1.6×10^{-2} (b) 1.6×10^{-5}
(c) 1.6×10^{-3} (d) 1.6×10^{-4}
(e) 1.6×10^{-1}

22. The pH of a saturated solution of a metal hydroxide of formula $X(OH)_2$ is 12.0 at 298 K. What is the solubility product of the metal hydroxide at 298 K (in mol^3 L^{-3})?
(a) 2×10^{-6} (b) 1×10^{-7}
(c) 5×10^{-5} (d) 2×10^{-5}
(e) 5×10^{-7}

23. An aqueous solution containing 3 g of a solute of molar mass 111.6 g mol^{-1} in a certain mass of water freezes at – 0.125 °C. The mass of water in grams present in the solution is
(K_f = 1.86 K kg mol^{-1})
(a) 300 (b) 600
(c) 500 (d) 400
(e) 250

24. A sample of sea water contains 5×10^{-3} g of dissolved oxygen in 1 kilogram of the sample. The concentration of O_2 in that sea water sample in ppm is
(a) 5×10^{-4} (b) 5×10^{-3}
(c) 5×10^{-2} (d) 5×10^{-1}
(e) 5

25. The change in potential of the half-cell $Cu^{2+}|Cu$, when aqueous Cu^{2+} solution is diluted 100 times at 298 K? $\left(\frac{2.303\,RT}{F} = 0.06\right)$
(a) Increases by 120 mV
(b) Decreases by 120 mV
(c) Increases by 60 mV
(d) Decreases by 60 mV
(e) No change

26. Consider the following electrolytic cells :
(i) $M_{(s)} \mid M^{2+}_{(aq)}$, 0.1 M $\| X^{2+}_{(aq)}$, 0.01 M $\mid X_{(s)}$
(ii) $M_{(s)} \mid M^{2+}_{(aq)}$, 0.1 M $\| X^{2+}_{(aq)}$, 0.1 M $\mid X_{(s)}$ and
(iii) $M_{(s)} \mid M^{2+}_{(aq)}$, 0.01 M $\| X^{2+}_{(aq)}$, 0.1 M $\mid X_{(s)}$
(a) $E_1 > E_2 > E_3$ (b) $E_2 > E_3 > E_1$
(c) $E_3 > E_1 > E_2$ (d) $E_1 > E_3 > E_2$
(e) $E_3 > E_2 > E_1$

27. In a reaction $2A + B \longrightarrow 3C$, the concentration of A decreases from 0.5 mol L^{-1} to 0.3 mol L^{-1} in 10 minutes. The rate of production of 'C' during this period is
(a) 0.01 mol L^{-1} min^{-1}
(b) 0.04 mol L^{-1} min^{-1}
(c) 0.05 mol L^{-1} min^{-1}
(d) 0.03 mol L^{-1} min^{-1}
(e) 0.02 mol L^{-1} min^{-1}

28. Ammonium ion (NH_4^+) reacts with nitrite ion (NO_2^-) in aqueous solution according to the equation :
$NH_{4(aq)}^+ + NO_{2(aq)}^- \longrightarrow N_{2(g)} + 2H_2O_{(l)}$
The following initial rates of reaction have been measured for the given reactant concentrations.

Expt. No.	$[NH_4^+]$, (M)	$[NO_2^-]$, (M)	Rate (M/hr)
1	0.010	0.020	0.020
2	0.015	0.020	0.030
3	0.010	0.010	0.005

Which of the following is the rate law for this reaction?
(a) rate = $k\,[NH_4^+]\,[NO_2^-]^4$
(b) rate = $k\,[NH_4^+]\,[NO_2^-]$
(c) rate = $k\,[NH_4^+]\,[NO_2^-]^2$
(d) rate = $k\,[NH_4^+]^2\,[NO_2^-]$
(e) rate = $k\,[NH_4^+]^{1/2}\,[NO_2^-]^{1/4}$

29. Gold sol can be prepared by
(a) hydrolysis of gold(III) chloride
(b) oxidation of gold by aqua regia
(c) peptization
(d) treating gold(III) chloride with metallic zinc
(e) reduction of gold(III) chloride with formalin solution.

30. The IUPAC name of the complex $[Co(NH_3)_2(H_2O)_4]Cl_3$ is
(a) diaminetetraaquacobalt(III) trichloride
(b) diaminetetraaquacobalt(II) chloride
(c) diaminetetraaquacobalt(III) chloride
(d) tetraaquadiaminecobalt(III) trichloride
(e) tetraaquadiaminecobalt(II) chloride.

31. The products obtained by the ozonolysis of 2-ethylbut-1-ene are
(a) propanone and ethanal
(b) ethanal and 3-pentanone
(c) butanal and ethanal
(d) methanal and 2-pentanone
(e) methanal and 3-pentanone.

32. When but-2-yne is treated with Na in liquid ammonia
(a) *cis*-2-butene is obtained
(b) *trans*-2-butene is formed
(c) *n*-butane is the major product
(d) it rearranges to but-1-yne
(e) there is no reaction.

33. The correct decreasing order of reactivity for a given alkyl (*R*) group in both S_N1 and S_N2 reactioin mechanisms is
(a) $R - I > R - Br > R - Cl > R - F$
(b) $R - I > R - Cl > R - Br > R - F$
(c) $R - F > R - Cl > R - Br > R - I$
(d) $R - F > R - I > R - Cl > R - Br$
(e) $R - Br > R - I > R - F > R - Cl$

34. The compound of molecular formula $C_5H_{10}O$ (*A*) reacts with Tollens' reagent to give silver mirror but does not undergo aldol condensation. The compound *A* is
(a) 3-pentanone
(b) 2, 2-dimethylpropanal
(c) 3-hydroxy-2-pentene
(d) 3-methylbutanal
(e) 3-methyl-2-butanone.

35. When *n*-hexane is heated with anhydrous $AlCl_3$ and HCl gas, the major product obtained is
(a) 1-chlorohexane (b) 2-chlorohexane
(c) 3-chlorohexane (d) hex-3-ene
(e) mixture of 2-methylpentane and 3-methylpentane.

36. How many monochloro structural isomers are expected in free radical monochlorination of 2-methylbutane?
(a) 2 (b) 3
(c) 4 (d) 5
(e) 6

37. Chloroform reacts with oxygen in the presence of light to give
(a) carbon tetrachloride
(b) carbonyl chloride
(c) methyl chloride
(d) methylene dichloride
(e) acetaldehyde.

38. Which one of the following is not expected to undergo iodoform reaction?
(a) Propan-2-ol (b) 1-Phenylethanol
(c) 2-Butanol (d) Ethanol
(e) Diphenyl methanol

39. Identify the combination of compounds that undergo Aldol condensation followed by dehydration to produce but-2-enal.
(a) Methanal and ethanal
(b) Two moles of ethanal
(c) Methanal and propanone
(d) Ethanal and propanone
(e) Two moles of ethanol.

40. The correct increasing order of the acid strength of benzoic acid (I), 4-nitrobenzoic acid (II), 3,4-dinitrobenzoic acid (III) and 4-methoxybenzoic acid (IV) is
(a) I < II < III < IV (b) II < I < IV < III
(c) IV < I < II < III (d) IV < II < I < III
(e) I < IV < II < III

41. An organic compound with the molecular formula C_8H_8O forms 2,4-DNP derivative, reduces Tollens' reagent and undergoes Cannizzaro reaction. On vigorous oxidation, it gives 1,2-benzenedicarboxylic acid. The organic compound is
(a) 2-ethylbenzaldehyde
(b) 2-methylbenzaldehyde
(c) acetophenone
(d) 3-methylbenzaldehyde
(e) phenylacetaldehyde.

42. Phenyl isocyanide is prepared from aniline by
(a) Rosenmund's reaction
(b) Kolbe's reaction
(c) Reimer—Tiemann reaction
(d) Wurtz reaction
(e) Carbylamine reaction.

43. Choose the correct order of decreasing basic strength of the following compounds in aqueous solution :

(i) $C_6H_5NH_2$ (ii) $C_2H_5NH_2$
(iii) NH_3 (iv) $(CH_3)_2NH$
(a) (i) > (ii) > (iii) > (iv)
(b) (iv) > (ii) > (iii) > (i)
(c) (ii) > (i) > (iii) > (iv)
(d) (iv) > (iii) > (ii) > (i)
(e) (ii) > (iv) > (iii) > (i)

44. Gabriel's phthalimide synthesis can be used to prepare
(a) ethanamine
(b) *N*-methylmethanamine
(c) benzeneamine
(d) *N*, *N*-dimethylmethanamine
(e) *p*-toluidine.

45. The sugar moiety present in RNA molecule is
(a) β-*D*-2-deoxyribose
(b) β-*D*-galactose
(c) β-*D*-fructofuranose
(d) β-*D*-ribose
(e) β-*D*-glucopyranose.

46. Novolac, the linear polymer used in paints is
(a) copolymer of 1, 3-butadiene and styrene
(b) obtained by the polymerization of methyl methacrylate
(c) initial product obtained in the condensation of phenol and formaldehyde in the presence of acid catalyst
(d) obtained by the polymerization of caprolactam
(e) copolymer of melamine and formaldehyde.

47. The carbohydrate used as storage molecules in animals is
(a) sucrose (b) glycogen
(c) maltose (d) glucose
(e) fructose.

48. Green chemistry deals with
(a) study of plant physiology
(b) study of extraction of natural products from plants
(c) detailed study of reactions involved in the synthesis of chlorophyll
(d) utilization of existing knowledge base for reducing the chemical hazards along with developmental activities
(e) synthesis of chemical compounds using green light.

SOLUTIONS

1. (c) : Energy of one photon $= \frac{hc}{\lambda}$

$$= \frac{6.626\times10^{-34}\times3\times10^{8}}{6626\times10^{-10}} = 3\times10^{-19}\ \text{J}$$

Energy emitted by bulb $= \frac{250\times80}{100} = 200\ \text{J}$

$\therefore \quad n \times 3 \times 10^{-19} = 200$ J

where n = no. of photons

$$n = \frac{200}{3\times10^{-19}} = 6.66\times10^{20}$$

2. (d) : $\overline{\upsilon} = \frac{1}{\lambda} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$

For Lyman series, $n_1 = 1$ and $n_2 = \infty$

then, $\frac{1}{\lambda} = R_H\left(\frac{1}{(1)^2} - \frac{1}{\infty}\right)$

or, $\lambda = \frac{1}{R_H}$ or $\lambda = \frac{1}{109678}$

$= 911.7 \times 10^{-8}$ cm $= 911.7$ Å

3. (e) : $K.E. = h\upsilon - h\upsilon_0 = 6.2 - 5.0 = 1.2$ eV

1 eV $= 1.6 \times 10^{-19}$ J

then 1.2 eV $= 1.2 \times 1.6 \times 10^{-19}$ J

$= 1.92 \times 10^{-19}$ J

4. (b) : Lattice energy is the energy required to separate 1 mole of an ionic compound into its ions in gaseous state.

$NaCl_{(s)} \longrightarrow Na^+_{(g)} + Cl^-_{(g)}$;

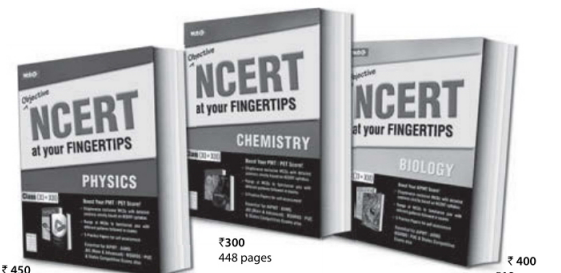
$\Delta_{lattice}H^\circ = 788\ \text{kJ mol}^{-1}$

5. (c) : $\text{B.O.} = \frac{1}{2}(N_b - N_a)$

Molecules/ ions	Total no. of electrons	M.O. configuration	B.O.
C_2	12	$\sigma1s^2, \sigma^*1s^2, \sigma2s^2, \sigma^*2s^2, (\pi2p_x^2 = \pi2p_y^2)$	2.0
Li_2	6	$\sigma1s^2, \sigma^*1s^2, \sigma2s^2$	1.0
O_2^+	15	$\sigma1s^2, \sigma^*1s^2, \sigma2s^2, \sigma^*2s^2, \sigma2p_z^2, (\pi2p_x^2 = \pi2p_y^2), (\pi^*2p_x^1 = \pi^*2p_y^0)$	2.5
He_2^+	3	$\sigma1s^2, \sigma^*1s^1$	0.5

Hence, the correct order of their stability is :
$He_2^+ < Li_2 < C_2 < O_2^+$.

How to select the correct answer faster?



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6. (b) : SF_4 has see-saw shape.

7. (c)

8. (a) : From ideal gas equation, $PV = nRT$

$$P = \frac{nRT}{V} = \frac{2 \times 0.082 \times 500}{41} = 2 \text{ atm}$$

9. (a) : From ideal gas equation, $PV = nRT$

$$PV = \frac{w}{M}RT \qquad \left(\because \quad n = \frac{w}{M}\right)$$

so, $P \propto \frac{1}{M}$

$$\therefore \quad \frac{P_1}{P_2} = \frac{M_2}{M_1}$$

$$\Rightarrow \quad \frac{2}{5} = \frac{32}{M_1} \quad \text{or,} \quad M_1 = \frac{5 \times 32}{2} = 80 \text{ g mol}^{-1}$$

10. (c) : Hydroformylation or oxo process is an important catalyzed industrial process for the production of only aldehydes from alkenes.

11. (d) :

S. No.	Species	No. of electrons
(i)	NH_3	10
(ii)	CH_3^+	8
(iii)	NH_2^-	10
(iv)	NH_4^+	10

Hence, the isoelectronic species are (i), (iii) and (iv).

12. (a) : Potassium (K) and their salts gives violet colour in the flame.

$$K_2SO_4 + BaCl_2 \longrightarrow \underset{\text{white ppt.}}{BaSO_4\downarrow} + 2KCl$$

13. (a) : Using formula, $H = \frac{1}{2}(V + M - C + A)$

[where, V = no. of electrons in valence shell, M = no. of monovalent atoms, C = charge on cation, A = charge on anion, H = no. of orbitals involved.]

Species	V	M	C	A	H	Hybridization
NH_4^+	5	4	1	0	4	sp^3
BF_3	3	3	0	0	3	sp^2
SF_6	6	6	0	0	6	sp^3d^2
PCl_5	5	5	0	0	5	sp^3d
XeF_4	8	4	0	0	6	sp^3d^2 (2 lone pairs of electrons)

14. (d) : All interhalogen compounds are diamagnetic in nature.

15. (d) : The two oxygen-oxygen bond lengths in the ozone molecule are same *i.e.* 1.278 Å.

16. (b) : Oxidation state of Mn in MnO_4^- is

$x + 4(-2) = -1 \quad \Rightarrow \quad x = +7$

Oxidation state of Cr in $Cr_2O_7^{2-}$ is

$2x + 7(-2) = -2 \Rightarrow \quad x = +6$

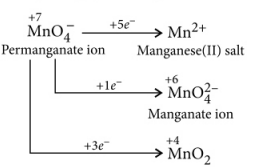
Oxidation state of V in VO_2^+ is

$x + 2(-2) = +1 \quad \Rightarrow \quad x = +5$

Hence, the correct descending order of oxidizing power is :

$MnO_4^- > Cr_2O_7^{2-} > VO_2^+$.

17. (a) :



18. (a) : For divalent ion, $M^{2+}(Z = 24)$, [Ar] $3d^4 4s^0$

Using formula, $\mu = \sqrt{n(n+2)}$ B.M.

(where, n = no. of unpaired electrons)

$\mu = \sqrt{4(4+2)} = 4.89 \sim 4.90$ B.M.

19. (a) : $X_{(l)} \longrightarrow X_{(g)}$; $\Delta S_{\text{vaporization}} = 58 \text{ J K}^{-1} \text{ mol}^{-1}$

For $X_{(g)} \longrightarrow X_{(l)}$; $\Delta S_{\text{condensation}} = ?$

$$\Delta S_{\text{condensation}} = \frac{100}{58} \times -58 = -100 \text{ J K}^{-1}$$

20. (e) : $\Lambda^{\circ}_{m(HCOOH)} = \lambda^{\circ}_{H^+} + \lambda^{\circ}_{HCOO^-}$

$= 347 + 53$

$= 400\ S\ cm^2\ mol^{-1}$

Degree of dissociation, $\alpha = \frac{\Lambda^c_m}{\Lambda^{\circ}_m} = \frac{40}{400} = 0.1$

So, dissociation constant,

$K_a = c\alpha^2$ (for weak electrolytes)

$= 0.025 \times (0.1)^2 = 2.5 \times 10^{-4}$

21. (c) : For equation, $A_{2(s)} \rightleftharpoons B_{2(s)} + 2C_{(g)}$

at equilibrium,

no. of moles of $C = \frac{1}{50} \times 2 = 0.04$ moles

Applying ideal gas equation, $PV = nRT$

$P \times 24.6 = 0.04 \times 0.082 \times 300$

$P = \frac{0.04 \times 0.082 \times 300}{24.6} = 0.04$ atm

$K_p = P_C^2 = (0.04)^2 = 1.6 \times 10^{-3}$ atm^2

22. (e) : $X(OH)_2 \rightleftharpoons X^{2+} + 2OH^-$ … (i)

$K_{sp} = [X^{2+}]\ [OH^-]^2$ … (ii)

pH + pOH = 14

12 + pOH = 14 $\Rightarrow$ pOH = 2

pOH = $-\log[OH^-]$

$2 = -\log[OH^-]$

$[OH^-] = 1 \times 10^{-2}$

From the chemical equation (i), the $[X^{2+}]$ is half of the $[OH^-]$ ion, therefore,

$[X^{2+}] = \frac{1 \times 10^{-2}}{2} = 5 \times 10^{-3}$

Now, putting the value of $[OH^-]$ and $[X^{2+}]$ ions in eqn. (ii), we get

$K_{sp} = [X^{2+}]\ [OH^-]^2 = (5 \times 10^{-3})(1 \times 10^{-2})^2$

$= 5 \times 10^{-3} \times 1 \times 10^{-4} = 5 \times 10^{-7}$

23. (d) : $\Delta T_f = \frac{1000 \times K_f \times w}{W \times M}$ … (i)

Given, $K_f = 1.86$ K kg mol^{-1}, $w = 3$ g, $W = ?$

$M = 111.6$ g mol^{-1}, $T_f = -0.125$ °C

$\Delta T_f = T_f^{\circ} - T_f = 0$ °C $- (-0.125$ °C$) = 0.125$ °C

On putting the values in eqn. (i), we get

$0.125 = \frac{1000 \times 1.86 \times 3}{W \times 111.6}$

$W = \frac{1000 \times 1.86 \times 3}{0.125 \times 111.6} = 400$ g

24. (e) : Dissolved oxygen $= 5 \times 10^{-3}$ g

$= 5$ mg/kg sea water

$\therefore$ Concentration of O_2 (in ppm) = 5 ppm

25. (d) : decreases by 60 mV

26. (e) : The chemical reaction is as

$M_{(s)} + X^{2+}_{(aq)} \rightleftharpoons M^{2+}_{(aq)} + X_{(s)}$

Applying the Nernst equation,

$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{n} \log \frac{[M^{2+}]}{[X^{2+}]}$

or, $E_{cell} = E^{\circ}_{cell} + \frac{0.0591}{n} \log \frac{[X^{2+}]}{[M^{2+}]}$

$E_1 = E^{\circ}_{cell} + \frac{0.0591}{2} \log \frac{0.01}{0.1}$

$= E^{\circ}_{cell} + 0.02955(-1)$

$\therefore \quad E_1 = E^{\circ}_{cell} - 0.02955$

$E_2 = E^{\circ}_{cell} + 0.02955 \log \left(\frac{0.1}{0.1}\right)$

$\therefore \quad E_2 = E^{\circ}_{cell} \quad [\because \log 1 = 0]$

$E_3 = E^{\circ}_{cell} + 0.0295 \log \left(\frac{0.1}{0.01}\right)$

$\therefore \quad E_3 = E^{\circ}_{cell} + 0.0295$

Thus, $E_3 > E_2 < E_1$

27. (d) : For the reaction, $2A + B \longrightarrow 3C$

The rate law is, $-\frac{1}{2}\frac{d[A]}{dt} = \frac{d[B]}{dt} = \frac{1}{3}\frac{d[C]}{dt}$

The concentration of A decreases,

$0.5 - 0.3 = 0.2$ mol L^{-1}

So, $-\frac{d[A]}{dt} = \frac{0.2 \text{ mol L}^{-1}}{10 \text{ min}} = 0.02$ mol L^{-1} min^{-1}

and $\frac{d[C]}{dt} = \frac{3}{2}\left(-\frac{d[A]}{dt}\right) = \frac{3}{2} \times 0.02$

$= 0.03$ mol L^{-1} min^{-1}

28. (c) : $NH_{4(aq)}^{+} + NO_{2(aq)}^{-} \longrightarrow N_{2(g)} + 2H_2O_{(l)}$

Let the rate law be,

Rate $= k[NH_4^+]^x\ [NO_2^-]^y$ … (I)

From expt. (1), $0.02 = k(0.01)^x\ (0.02)^y$ … (i)

From expt. (2), $0.03 = k(0.015)^x\ (0.02)^y$ … (ii)

Dividing equation (ii) by (i), we get

$\frac{0.03}{0.02} = \frac{k(0.015)^x (0.02)^y}{k(0.01)^x (0.02)^y}$

$(1.5)^1 = (1.5)^x \Rightarrow x = 1$

From expt. (3), $0.005 = k(0.01)^x\ (0.01)^y$ … (iii)

Dividing equation (iii) by (i), we get

$$\frac{0.005}{0.02} = \frac{k(0.01)^x(0.01)^y}{k(0.01)^x(0.02)^y}$$

$(0.25)^x = (0.5)^y$ or $(0.5)^2 = (0.5)^y$

$\Rightarrow \quad y = 2$

Now, putting the values of x and y in eqn. (I), we get

$$\text{rate} = k[NH_4^+]^1\,[NO_2^-]^2$$

29. (e) : $2AuCl_3 + 3HCHO + 3H_2O \xrightarrow{\text{Reduction}} 2Au + 3HCOOH + 6HCl$ (sol)

30. (c)

31. (e) : $H_3C-CH_2-\underset{\underset{CH_2CH_3}{|}}{C}=CH_2 \xrightarrow[\text{(ii) } Zn/H_2O]{\text{(i) } O_3 \text{ (ozonolysis)}}$

2-Ethylbut-1-ene

$HCHO + H_3C-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$

Methanal 3-Pentanone

32. (b) : $CH_3-C\equiv C-CH_3 + 2Na \xrightarrow{\text{liq. } NH_3}$

But-2-yne

$$\begin{matrix} H_3C & & H \\ & \diagdown & / \\ & C=C & \\ & / & \diagdown \\ H & & CH_3 \end{matrix} + 2NaNH_2$$

trans-2-butene

33. (a) : $\underset{\text{(most reactive)}}{R-I} > R-Br > R-Cl > \underset{\text{(least reactive)}}{R-F}$

$C-X$ bond strength increases

Smaller the energy required for cleaving C—I bond, better is the leaving group (I^-) and faster is the rate of reaction.

34. (b) : $H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CHO \xrightarrow{\text{Tollens' reagent, } Ag_2O/NH_4OH,\ \Delta}$

2,2-Dimethylpropanal ($C_5H_{10}O$) (*A*)

$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-COO^- + Ag\downarrow$ Silver mirror

2,2-Dimethylpropanoate ion

Since, 2,2-dimethylpropanal does not contain α-hydrogen, hence does not undergo aldol condensation.

35. (e) : *n*-Hexane $\xrightarrow[\Delta]{\text{anhy. } AlCl_3 + HCl_{(g)}}$ (Isomerisation)

2-Methylpentane + 2,3-Dimethylbutane

3-Methylpentane + 2,2-Dimethylbutane

36. (c) : $H_3C-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$

2-Methylbutane

$\xrightarrow[Cl_2]{h\upsilon}$

- $H_3C-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2Cl$ — 2-Methyl-1-chlorobutane
- $H_3C-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{Cl}{|}}{C}}-CH_3$ — 2-Methyl-2-chlorobutane
- $H_3C-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{Cl}{|}}{CH}-CH_3$ — 3-Methyl-2-chlorobutane
- $H_3C-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_2Cl$ — 3-Methyl-1-chlorobutane

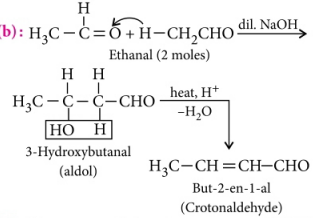
37. (b) : $\underset{\text{Chloroform}}{CHCl_3} + O_2 \xrightarrow[\text{and air}]{\text{light}} \underset{}{COCl_2} + HCl$

Carbonyl chloride (Phosgene)

38. (e) : Alcohols of the type CH_3–CHOH–*R* (where, *R* = H/alkyl/aryl group) undergo iodoform reaction.

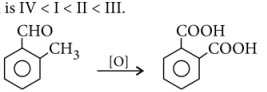
But, diphenyl methanol (C_6H_5–CHOH–C_6H_5) does not undergo iodoform reaction.

39. (b):



40. (c): Electron withdrawing group ($-NO_2$) present in benzoic acid increases the acidic strength while electron releasing group ($-OCH_3$) decreases the acidic strength. Hence, the correct increasing order of the acidic strength is IV < I < II < III.

41. (b):



2-Methylbenzaldehyde (C_8H_8O) 1,2-Benzenedicarboxylic acid

42. (e): In carbylamine reaction,

$$C_6H_5NH_2 + CHCl_3 + 3KOH_{(alc.)} \xrightarrow{\Delta} C_6H_5NC + 3KCl + 3H_2O$$

43. (b): Because of combined +*I* effect of the alkyl group, steric hindrance and the solvation of amines, the basicity of 2° amine is more than 1° amine and ammonia.

In aniline, the unshared electron pair on nitrogen atom is in conjugation with the benzene ring and thus is less available for donation.

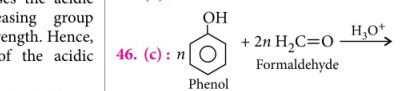
Hence, the correct decreasing order is :

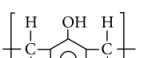
$(CH_3)_2NH > C_2H_5NH_2 > NH_3 > C_6H_5NH_2$
(iv) (ii) (iii) (i)

44. (a): Only aliphatic 1° amine (ethanamine) can be prepared by Gabriel's phthalimide synthesis.

45. (d)

46. (c):





Novolac

47. (b): Glycogen stored in liver and muscles acts as the reserve food material in animals. It is also known as 'animal starch'.

48. (d)

ADVANCED CHEMISTRY BLOC

(POLYMORPHISM AND CRYSTAL DEFECTS)

Mukul C. Ray, Odisha

Certain topics present in the syllabus raise various questions while reading and teaching chemistry. This advanced bloc in chemistry will bring few of those topics with slightly advanced level discussion to clarify those curiosities. The overall idea is not to rewrite those things, which are there in the book, but to present explanation, important points and to raise interest in chemistry reading. By the way we may ignore some ordinary points.

Solid state is there in the beginning of the class-XII syllabus. Besides the unit cells, lattice parameters, voids, packing efficiency we have one more area called as polymorphism. For example, ice crystallizes in hexagonal as well as cubic unit cells.

Polymorphs

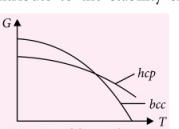
Many metals or compounds can crystallize in different forms depending on temperature - they exhibit the phenomenon of polymorphism. Around 30 metals such as Fe, U, Cr, Co, V, Sn, etc. exhibit this phenomenon. The polymorphs of elements are designated by Greek letters α, β, γ etc. The α form is the one, more stable at low temperature.

The stability of different forms at definite temperatures and pressures is determined by the thermodynamic potential (G).

$$G = H - TS$$

The modification having lower algebraic value of thermodynamic potential at a given temperature is the most stable form at that temperature, which is achieved by either lowering the enthalpy or increasing the entropy.

A *fcc* or *hcp* crystal structure with higher co-ordination number 12 enjoys extra attraction forces and hence have a lower enthalpy. On the contrary, such tight packing lowers chaos or disorderness. This means in *fcc* or *hcp*, enthalpy supports stability better but entropy factor does not contribute to the stability much. When we have *bcc* structure, the co-ordination number is reduced to 8 – a less packed arrangement; so naturally enthalpy does not contribute to the stability significantly.



Variation of thermodynamic potential of *hcp* and *bcc* forms with temperature

But due to lose packing, entropy is now more. Higher temperature now can make lower value of 'G'. Therefore, *bcc* form of crystals are stabilized at higher temperature (Note Fe is an exception-*bcc* is stable at lower temperature surely due to some additional entropy contributions).

Examples:

- Fe exists as *bcc* at any temperature below 912 °C (α-form). Between 912 °C to 1394 °C, iron has *fcc* structure (γ-form). Under very high pressure iron turns to *hcp* form.
- Ice crystallizes in hexagonal form under normal conditions but at very low temperature gives cubic crystal.
- Usually available tin is the white tin (β-form). It has a body centered tetragonal structure with

co-ordination number 8. At low temperature, around 13 °C, it slowly transforms to gray tin (α-form). This form has diamond like structure with co-ordination number 4. This α-form of tin is fragile in nature.

- Calcium carbonate crystallizes in three different forms, calcite, vaterite and aragonite. Calcite is the most stable form.

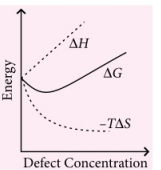
Crystal Defects

All crystals at a temperature above absolute zero have some point defects, means they have either some lattice points, which are vacant or containing some impurities. Up to a certain concentration the presence of point defects actually lower the free energy of the crystal and is thus favourable. The Gibbs free energy (G) of a crystal is a thermodynamic quantity that attains a minimum value when the crystal is in equilibrium with its surroundings. It is defined by the expression :

$$G = H - TS$$

The term H defines the internal energy at constant pressure. It is actually the electrostatic energy terms due to attraction forces and kinetic energy terms due to vibration of particles. The entropy (S) is the state of disorder in the crystal and T is the temperature.

Due to defects the bonding requirements are not well satisfied. Creation of defects requires energy and the enthalpy of the crystal increases. But at the same time entropy increases as defects create chaos in an otherwise perfect crystal.

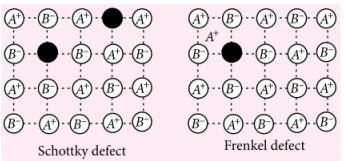


For a small defect in concentration, entropy increase and enthalpy increase are so adjusted that the system enjoys thermodynamic stability with minimum G. This is the equilibrium defect concentration at a particular temperature.

Schottky and Frenkel Defects

In stoichiometric compounds, these two defects are very common. The former, the Schottky is found in highly ionic compounds like NaCl, CsCl, KCl, etc. In Schottky defect, pairs of ions are missing from lattice points. Electrical neutrality is maintained and density decreases. Since less energy is required to create schottky defect than to break the crystal using lattice energy; this defect is very common. Frenkel defect is found in compounds where cation is relatively small in size than anion. It slips into the

interstitial position leaving the lattice point empty. It is therefore called as point defect, interstitial defect as well as vacancy defect.



Points to be noted are :

- Both these defects are responsible for lowering of lattice energy.
- Schottky defect is more common than Frenkel defect.
- Due to Frenkel defect, dielectric constant of the solid increases as the charges come closer.
- Due to both these defects, electrical conductivity of solid increases.
- AgBr shows both these defects.

Non-Stoichiometric Defects

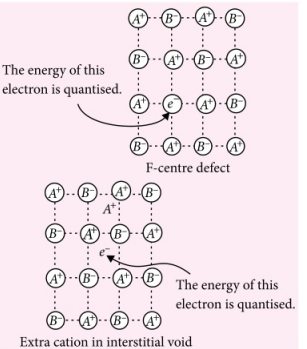
Metal deficiency and metal excess defects belong to this category. ZnO when heated reversibly lose oxygen and turns yellow.

$$ZnO \xrightarrow{\Delta} Zn^{2+} + \frac{1}{2}O_2 + 2e^-$$

The yellow ZnO turns white again when kept in atmospheric air as it absorbs oxygen.

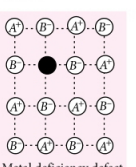
Similar is the case when NaCl solid is heated with vapours of sodium, it becomes yellow. The former is the case when the formula becomes $MO_{1-\delta x}$ and in the later case the formula becomes $M_{1+\delta x}Cl$.

In these defect-bearing solids the energy levels of electrons become quantised. They absorb visible light and hence become coloured. KCl when heated with vapours of potassium becomes blue/violet; LiCl when heated with vapours of lithium becomes pink. Naturally found calcium fluoride appears blue or violet due to F-centre defect.



There is another kind of defect where some of the cations are missing from the crystal lattice. For example, in FeO, there are some missing ferrous ions, which are neutralized when some of the existing ferrous ions become ferric. The compound now has the formula type $M_{1-\delta x}O$. NiO and FeS also show this kind of defects.

Due to these defects, the solid crystals exhibit slight better electrical conductivity. Logically we have another kind of defect possible which can be written as $MO_{1+\delta x}$. However, this kind of defect is not observed, as anions are too big to occupy interstitial positions.



EXAMINER'S MIND NCERT CLASS XII

The questions given in this column have been prepared strictly on the basis of NCERT Chemistry for Class XII. This year JEE (Main & Advanced)/AIPMT/AIIMS/other PMTs have drawn their papers heavily from NCERT books.

THE SOLID STATE | SOLUTIONS

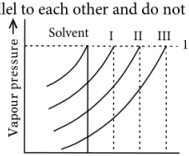
SECTION - I

Only One Option Correct Type

This section contains 20 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

1. A element has a body-centred cubic (*bcc*) structure with a cell edge of 288 pm. The density of the element is 7.2 g/cm^3. How many atoms are present in 208 g of the element?
(a) 6.02×10^{24} atoms
(b) 12.09×10^{23} atoms
(c) 24.16×10^{23} atoms
(d) 29.88×10^{24} atoms

2. The vapour pressure curves of the same solute in the same solvent are shown. The curves are parallel to each other and do not intersect.



The concentrations of solutions are in the correct increasing order of
(a) I < II < III (b) II < I < III
(c) III < I < II (d) III < II < I

3. Which of the following solids is not an electrical conductor?
(A) $Mg_{(s)}$ (B) $TiO_{(s)}$ (C) $I_{2(s)}$ (D) $H_2O_{(s)}$
(a) A only (b) B only
(c) C and D only (d) B, C and D only

4. Vapour pressure of C_6H_6 and C_7H_8 mixture at 50 °C is given by :
$P_{total} = 179\ x_B + 92$
(x_B = mole fraction of C_6H_6)
Then the vapour pressure of pure benzene in mm of Hg is
(a) 271 (b) 92
(c) 380 (d) 120

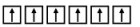
5. The composition of a sample of wustite is $Fe_{0.93}O_{1.00}$. The percentage of the ion present in the form of Fe (III) is
(a) 15.05 (b) 20.05
(c) 10.05 (d) 7.05

6. The degree of dissociation of $Ca(NO_3)_2$ in a dilute aqueous solution containing 14 g of salt per 200 g of water at 100 °C is 70%. If the vapour pressure of water at 100 °C is 760 mm, the vapour pressure of the solution would be
(a) 74.59 (b) 7.45
(c) 745.99 (d) 475.59

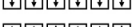
7. The freezing point of 0.1 M solution of glucose is –1.86 °C. If an equal volume of 0.3 M glucose solution is added, the freezing point of the mixture will be
(a) –7.44 °C (b) –5.58 °C
(c) –3.72 °C (d) – 2.79 °C

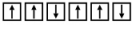
8. In the crystals of which of the following ionic compounds would you expect maximum distance between the centres of the cations and anions?
(a) LiF (b) CsF
(c) CsI (d) LiI

9. Which of the following arrangements shows schematic alignment of magnetic moments of antiferromagnetic substances?

(a) 

(b) 

(c) 

(d) 

10. Solution *A* contains 7 g/L $MgCl_2$ and solution *B* contains 7 g/L of NaCl. At room temperature, the osmotic pressure of

(a) solution *A* is greater than *B*
(b) both have same osmotic pressure
(c) solution *B* is greater than *A*
(d) can't determine.

11. If *A* is bivalent, *B* is trivalent cation, what is the formula of oxide having spinel structure if 1/8th of the tetrahedral voids and 1/2 of the octahedral voids are occupied?

(a) AB_2O_4 (b) A_2BO_4
(c) ABO_4 (d) $A_3B_2O_6$

12. For an ideal solution with $P_A^o > P_B^o$ which of the following is true?

(a) $(x_A)_{liquid} = (x_A)_{vapour}$
(b) $(x_A)_{liquid} > (x_A)_{vapour}$
(c) $(x_A)_{liquid} < (x_A)_{vapour}$
(d) There is no relationship between $(x_A)_{liquid}$ and $(x_A)_{vapour}$.

13. Which of the following statements is not true about NaCl structure?

(a) Each unit cell contains 4 NaCl molecules.
(b) Cl^- ions has coordination number six.
(c) Na^+ ions has coordination number four.
(d) Cl^- ions are in *fcc* arrangement.

14. Which of the following pairs shows a negative deviation from Raoult's law ?

(a) Acetone-benzene
(b) Acetone-ethanol
(c) Acetone-chloroform
(d) Benzene-methanol.

15. Na and Mg crystallise in *bcc* and *fcc* type crystals, then the number of Na and Mg atoms present in the unit cell of their respective crystal is

(a) 4 and 2 (b) 9 and 14
(c) 14 and 9 (d) 2 and 4

16. A semiconductor of Ge can be made *p*-type by adding

(a) trivalent impurity (b) tetravalent
(c) pentavalent (d) divalent impurity.

17. Raoult's Law is obeyed by a binary liquid solution when

(a) the forces of attractions between like molecules are greater than those between unlike molecules
(b) the forces of attractions between like molecules are smaller than those between unlike molecules
(c) the forces of attractions between like molecules are more or less identical with those between unlike molecules
(d) the volume occupied by unlike molecules are different.

18. If the same type of atoms are packed in hexagonal close packing (*hcp*) and cubical close packing (*ccp*) separately, then

(a) density of *hcp* will be greater than *ccp*
(b) density of *hcp* will be smaller than *ccp*
(c) density of *hcp* will be equal to *ccp*
(d) density of *hcp* may be equal or greater than or smaller than *ccp* depending upon the temperature of the system.

19. The relationship between osmotic pressure at 273 K when 10 g glucose (P_1), 10 g urea (P_2) and 10 g sucrose (P_3) are dissolved in 250 mL of water is

(a) $P_1 > P_2 > P_3$ (b) $P_3 > P_1 > P_2$
(c) $P_2 > P_1 > P_3$ (d) $P_2 > P_3 > P_1$

20. Vapour pressure of a solution of 5 g of non-electrolyte in 100 g of water at a particular temperature is 2985 N/m^2. The vapour pressure of pure water is 3000 N/m^2, the molecular weight of the solute is

(a) 90 (b) 200
(c) 180 (d) 380

SECTION - II

One or More Options Correct Type

This section contains 5 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONE or MORE are correct.

21. Which of the following statement(s) is/are not true?

(a) Vacancy defect results in a decrease in the density of the substance.
(b) Interstitial defect results in an increase in the density of the substance.
(c) Impurity defect has no effect on the density of the substance.
(d) Frenkel defect results in an increase in the density of the substance.

22. Which statement(s) is/are true about osmotic pressure (π), volume (V) and temperature (T)?

(a) $\pi \propto \frac{1}{V}$ if T is constant.
(b) $\pi \propto C$ if T is constant.
(c) $\pi \propto V$ if T is constant.
(d) π/C is constant if T is constant.

23. In a cubic lattice each edge of the unit cell is 400 pm. Atomic weight of the element is 60 and its density is 6.25 g/c.c. Avogadro number = 6×10^{23}. The crystal lattice is

(a) face-centred (b) primitive
(c) body-centred (d) end-centred.

24. The outer shell of an egg was dissolved in hydrochloric acid and then placed in concentrated NaCl solution. Which one of the following will happen?

(a) The egg will swell.
(b) The egg will shrink.
(c) Nothing will happen to the egg.
(d) The inside of the egg will become saltish.

25. Ferroelectricity is exhibited by

(a) barium titanate ($BaTiO_3$)
(b) potassium tartrate (Rochelle salt)
(c) potassium dihydrogen phosphate (KH_2PO_4)
(d) lead zirconate ($PbZrO_3$)

SECTION - III

Paragraph Type

This section contains 2 paragraphs each describing theory, experiment, data, etc. Six questions relate to two paragraphs with three questions on each paragraph. Each question of a paragraph has only one correct answer among the four choices (a), (b), (c) and (d).

Paragraph for Questions 26 to 28

Packing refers to the arrangement of constituent units in such a way that the forces of attraction among the constituent particles is maximum and the constituents occupy the maximum available space. In two dimensions, there are square close packing and hexagonal close packing. In three dimensions, however, there are hexagonal close packing, cubic close packing and body-centred cubic packing.

(i) *hcp* : *AB AB AB AB* .... arrangement
coordination number = 12
% occupied space = 74
(ii) *ccp* : *ABC ABC* ... arrangement
coordination number = 12
% occupied space = 74
(iii) *bcc* : 68% space is occupied
coordination number = 8

26. In a closed packed lattice containing n particles, the number of tetrahedral and octahedral voids are

(a) $n, 2n$ (b) n, n
(c) $2n, n$ (d) $2n, n/2$

27. The ratio of close packed atoms to tetrahedral holes in cubic close packing is

(a) 1 : 1 (b) 1 : 2
(c) 1 : 3 (d) 2 : 1

28. A certain oxide of metal M crystallises in such a way that O^{2-} ions occupy *hcp* arrangement following *AB AB* ... pattern. The metal ions, however, occupy $2/3^{rd}$ of the octahedral voids. The formula of the compound is

(a) M_2O_3 (b) M_3O
(c) $M_{8/3}O_3$ (d) MO_2

Paragraph for Questions 29 to 31

Ideal solutions obey Raoult's law while non-ideal solutions do not obey Raoult's law. Further ideal solutions do not show any volume change, enthalpy change, etc. on mixing whereas non-ideal solutions show a change in these properties. Based on their behaviour, non-ideal solutions are classified as those showing positive deviation and those showing negative deviation from ideal behaviour. For a particular composition, both form azeotropic mixtures.

29. Which of the following forms non-ideal solution?
(a) $C_2H_5I + C_2H_5Br$
(b) $C_4H_9Cl + C_4H_9Br$
(c) *n*-Hexane + *n*-Heptane
(d) $C_2H_5OH + CHCl_3$

30. Mixtures corresponding to maximum in boiling point curves show that
(a) they are azeotropic mixtures
(b) they show negative deviation from Raoult's law
(c) both (a) and (b)
(d) none of these.

31. A solution in which the solvent obeys Raoult's law and the solute obeys Henry's law is
(a) a perfectly ideal solution
(b) an ideal dilute solution
(c) both (a) and (b)
(d) neither (a) nor (b).

SECTION - IV

Matching List Type

This section contains 3 multiple choice questions. Each question has matching lists. The codes for the lists have choices (a), (b), (c) and (d), out of which ONLY one is correct.

32. Match the List I with the List II and select the correct answer using the code given below the lists :

	List I (Crystal defects)		List II (Structural features)
P.	F-centres	1.	Extra cations present in interstitial sites
Q.	Metal excess defect	2.	Some cations are replaced by ones of higher valency
R.	Metal deficiency defect	3.	Both cations and anions are missing from lattice sites.
S.	Schottky defects	4.	Electrons trapped in anionic vacancies

	P	Q	R	S
(a)	3	2	4	1
(b)	4	1	2	3
(c)	4	3	2	1
(d)	2	3	4	1

33. Match the List I with the List II and select the correct answer using the code given below the lists :

	List I (Items)		List II (Type of solutions)
P.	Soda water	1.	A solution of gas in gas
Q.	Sugar solution	2.	A solution of solid in liquid
R.	German silver	3.	A solution of solid in solid
S.	Air	4.	A solution of gas in liquid.

	P	Q	R	S
(a)	1	2	4	3
(b)	2	3	4	1
(c)	4	2	3	1
(d)	4	3	2	1

34. Match the List I with the List II and select the correct answer using the code given below the lists :

	List I (Axial parameters)		List II (Crystal system)
P.	$a \neq b \neq c$, $\alpha = \beta = \gamma = 90°$	1.	Triclinic
Q.	$a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90°$	2.	Hexagonal
R.	$a = b \neq c$, $\alpha = \beta = 90°$, $\gamma = 120°$	3.	Orthorhombic
S.	$a \neq b \neq c$, $\alpha = \gamma = 90° \neq \beta$	4.	Monoclinic

	P	Q	R	S
(a)	1	4	2	3
(b)	2	3	4	1
(c)	3	2	4	1
(d)	3	1	2	4

SECTION - V

Assertion-Reason Type

In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :

(a) If both assertion and reason are true and reason is the correct explanation of assertion.

(b) If both assertion and reason are true but reason is not the correct explanation of assertion.

(c) If assertion is true but reason is false.

(d) If both assertion and reason are false.

35. **Assertion :** Ferromagnetic property decreases as Fe > Co > Ni.
Reason : Ferromagnetic substances are attracted by magnetic field.

36. **Assertion :** 0.1 M solution of glucose has higher increment in the freezing point than 0.1 M solution of urea.
Reason : K_f for both has different values.

37. **Assertion :** Amorphous substances are isotropic.
Reason : Properties like refractive index, electrical conductance have different values in different direction for isotropic substances.

38. **Assertion :** The relative lowering of vapour pressure of a solution is equal to the mole fraction of the solute.

$$\frac{P^\circ - P}{P^\circ} = x_2$$

Reason : Raoult's law is applicable for all non-volatile electrolytes.

39. **Assertion :** In lattice of N atoms, the number of tetrahedral sites is $2N$.
Reason : The conductivity of insulator is equal to zero.

40. **Assertion :** Isotonic solutions must have the same molar concentrations.
Reason : Solutions which have the same osmotic pressure at the same temperature are known as isotonic solutions.

SECTION - VI

Integer Value Correct Type

This section contains 10 questions. The answer to each question is a single digit integer, ranging from 0 to 9 (both inclusive).

41. The packing fraction of the element that crystallises in simple cubic arrangement is π/x. The value of x is

42. Molarity of a given orthophosphoric acid solution is 3 M. Its normality is

43. Structure of CsBr is same as of CsCl. The total number of Cs^+ ion is

44. Among the given solutions, the total number of isotonic solutions is
0.15 M urea, 0.05 M $CaCl_2$, 0.1 M $MgSO_4$, 0.15 M glucose

45. The density of crystalline sodium chloride is 2.165 g cm^{-3}. Dimension of cube containing one mole of NaCl is

46. A solution containing 0.1 g of a non-volatile organic substance P (molecular mass 100) in 100 g of benzene raises the boiling point of benzene by 0.2 °C, while a solution containing 0.1 g of another non-volatile substance Q in the same amount of benzene raises the boiling point of benzene by 0.4 °C. The ratio of molecular masses of P and Q is $x : 1$ where x is

47. AB crystallises in a rock salt structure with $A : B = 1 : 1$. The shortest distance between A and B is $Y^{1/3}$ nm. The formula mass of AB is 6.023 Y a.m.u. where Y is an arbitrary constant. The density (in kg m^{-3}) is

48. The vapour pressures of pure liquids A and B are 450 and 700 mm Hg at 350 K respectively. Total vapour pressure of liquid mixture is 600 mm Hg. If the mole fraction of B is $(x/10)$, then the value of x is

49. The coordination number of Al in the crystalline state of $AlCl_3$ is

50. The osmotic pressure of a urea solution is 500 mm of Hg at 10 °C. The solution is dilute and its temperature is raised to 25 °C. It is now found that osmotic pressure of the solution is reduced to 105.3 mm of Hg. The extent of dilution of the solution is

SOLUTIONS

1. (c) : Volume of the unit cell = $(288\ pm)^3$
$= (288 \times 10^{-12}\ m) = (288 \times 10^{-10}\ cm)^3$
$= 2.39 \times 10^{-23}\ cm^3$
Volume of 208 g of the element
$= \dfrac{mass}{density} = \dfrac{208\ g}{7.2\ g\ cm^{-3}} = 28.88\ cm^3$
Number of unit cells in this volume
$= \dfrac{28.88\ cm^3}{2.39 \times 10^{-23}\ cm^3 / unit\ cell}$
$= 12.08 \times 10^{23}$ unit cells
Since each *bcc* unit cell contains 2 atoms, therefore, the total number of atoms in 208 g
$= 2(atoms/unit\ cell) \times 12.08 \times 10^{23}$ unit cells
$= 24.16 \times 10^{23}$ atoms.

2. (a) : As the concentration of non-volatile solute increases, vapour pressure is lowered and boiling point increases.
Hence, order is I < II < III.

3. (c) : $I_{2(s)}$ and $H_2O_{(s)}$ are bad conductors of electricity.

4. (a) : $P_{total} = 179\ x_B + 92$
For a binary volatile liquid mixture,
$P_{total} = P_B^o x_B + P_T^o x_T$
$P_B^o \rightarrow$ pressure of pure benzene
$x_B \rightarrow$ mole fraction of benzene
$P_T^o \rightarrow$ pressure of pure toluene
$x_T \rightarrow$ mole fraction of toluene
$P_{total} = P_B^o x_B + P_T^o (1 - x_B) = P_B^o x_B + P_T^o - P_T^o x_B$
$179 x_B + 92 = (P_B^o - P_T^o) x_B + P_T^o$
Thus $P_T^o = 92$
$P_B^o - P_T^o = 179 \Rightarrow P_B^o = 179 + 92 = 271$ mm of Hg

5. (a) : The compound $Fe_{0.93}O_{1.00}$ is non-stoichiometric where electrical neutrality is achieved by converting appropriate Fe^{2+} ions into Fe^{3+} ions.
There are 7 Fe^{2+} ions missing out of the expected 100 Fe^{2+} ions. The missing 2×7 positive charge is compensated by the presence of Fe^{3+} ions. Replacement of one Fe^{2+} ion by Fe^{3+} ion increases one positive charge.
Thus, 14 positive charges are compensated by the presence of 14 Fe^{3+} ions out of a total of 93 Fe ions.
Hence, % of Fe^{3+} ions present
$= \dfrac{14}{93} \times 100 = 15.05$

6. (c) :

	$Ca(NO_3)_2 \rightleftharpoons$	Ca^{2+}	+	$2NO_3^-$
Initial conc.	1	0		0
Equili. conc.	1 – 0.7	0.7		1.4

$\dfrac{\text{Number of particles after dissociation}}{\text{Number of particles before dissociation}} = \dfrac{\text{Normal mol. wt.}}{\text{Observed mol. wt.}}$
$\dfrac{2.4}{1} = \dfrac{164}{M_1}$ or $M_1 = 68.33$
According to Raoult's law,
$\dfrac{P° - P_s}{P} = \dfrac{w_1 M_2}{w_2 M_1}$ or $\dfrac{760 - P_s}{760} = \dfrac{14 \times 18}{200 \times 68.33}$
$P_s = 745.99$ mm

7. (c) : $K_f = \Delta T_f / m = 1.86/0.1 = 18.6$
$M_1V_1 + M_2V_2 = M_3V_3$
$V_1 = V_2 = V$, $V_3 = (V + V) = 2V$
$0.1 \times V + 0.3 \times V = M_3 \times 2\ V$
or $M_3 = 0.2$, $\Delta T_f = 18.6 \times 0.2 = 3.72$ °C
$T_f = -3.72$ °C

8. (c) : Cs^+ and I^- ions have largest sizes.

9. (d) : Alignment of magnetic moments of antiferromagnetic solids is such that the resultant magnetic moment is zero.

10. (c) : 7 g L^{-1} $MgCl_2 = \dfrac{7}{24+71}$ mol L^{-1}
$= \dfrac{7}{95}$ mol $L^{-1} = \dfrac{7 \times 3}{95} = 0.22$ mol L^{-1} of ions
7 g L^{-1} NaCl $= \dfrac{7}{23 + 35.5}$ mol L^{-1}
$= \dfrac{7}{58.5}$ mol $L^{-1} = \dfrac{7 \times 2}{58.5} = 0.24$ mol L^{-1} of ions
As concentration of ions in NaCl solution is greater, NaCl solution (solution B) will have greater osmotic pressure.

11. (a) : In spinel structure, oxides are arranged in *ccp*, it means there are 4 atoms or ions per unit cell. Therefore, there are 4 octahedral voids and

8 tetrahedral voids. And dipositive ions occupy tetrahedral voids and tripositive ions occupy octahedral voids.

$\therefore$ Number of divalent ions, $A = 8 \times \frac{1}{8} = 1$

[only $\frac{1}{8}$ th tetrahedral voids are occupied]

$\therefore$ Number of trivalent ions, $B = \frac{1}{2} \times 4 = 2$

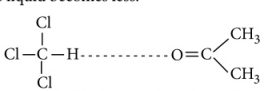
[$\frac{1}{2}$ of the octahedral voids are occupied]

Hence, formula of oxide having spinel structure is equal to AB_2O_4.

12. (c) : As A is more volatile, it would be richer in the vapour phase (by Konowaloff's rule). Hence, $(x_A)_{\text{vapour}} > (x_A)_{\text{liquid}}$.

13. (c) : Na^+ and Cl^- ions both have coordination number 6.

14. (c) : When acetone and chloroform are mixed, the hydrogen bonding takes place between the two due to which escaping tendency of either of the liquid becomes less.



Hydrogen bonding between chloroform and acetone

15. (d) : In *bcc*, number of atoms per unit cell = 2
In *fcc*, number of atoms per unit cell = 4.

16. (a) : *p*-type semiconductors are made by adding impurity of previous group elements. For making *p*-type semiconductor of Ge(14^{th} group), it is to be doped with trivalent impurity.

17. (c) : Ideal solutions obey Raoult's law where the intermolecular interactions between the different components ($A - B$ interactions) are of the same magnitude as the intermolecular interactions found in the pure components ($A - A$ and $B - B$ interactions).

18. (c) : Both *hcp* and *ccp* are equally efficient. Spheres occupy 74% of the possible space in both arrangements. Therefore, for same type of atoms, density will be same in *hcp* and *ccp*.

19. (c) : Molar concentration of glucose

$$= \frac{10}{180} \times \frac{1000}{250} = 0.22 \text{ M}$$

($\because$ Molecular weight of glucose = 180)

Molar concentration of urea

$$= \frac{10}{60} \times \frac{1000}{250} = 0.66 \text{ M}$$

($\because$ Molecular weight of urea = 60)

Molar concentration of sucrose

$$= \frac{10}{342} \times \frac{1000}{250} = 0.12 \text{ M}$$

($\because$ Molecular weight of sucrose = 342)

$\pi \propto C$

Thus, $P_2 > P_1 > P_3$.

20. (c) : $M_2 = \frac{w_2 M_1 \times P^\circ}{w_1 (P^\circ - P_s)}$

where, M_2 = molar mass of solute
w_2 = weight of solute
M_1 = molar mass of solvent
w_1 = weight of solvent
P^o = vapour pressure of pure solvent
P_s = vapour pressure of solution

$$M_2 = \frac{5 \times 18 \times 3000}{100 \times (3000 - 2985)} = 180$$

21. (c, d) : (c) is not true because impurity defect changes the mass but not the volume. (d) is not true because Frenkel defect neither changes mass nor volume.

22. (a, b, d) : $\pi \propto C$ (at constant T)

i.e. $\frac{\pi}{C}$ = constant (at constant T)

Again $C = \frac{n}{V}$ *i.e.* $C \propto \frac{1}{V}$ (at constant T)

i.e. $\pi \propto \frac{1}{V}$ (at constant T)

23. (a) : Let the number of atoms in the unit cell = x

Mass of x atoms in one unit cell $= \frac{60 \times x}{6 \times 10^{23}}$

Volume of the unit cell = $(\text{edge length})^3$
$= (400 \times 10^{-12} \times 100)^3 = (400 \times 10^{-10} \text{ cm})^3$
$= (4 \times 10^{-8} \text{ cm})^3 = 64 \times 10^{-24} \text{ cm}^3$

Density = 6.25 $= \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}}$

$$\therefore \quad 6.25 = \frac{60 \times x}{6 \times 10^{23} \times 64 \times 10^{-24}}$$

$$x = \frac{6.25 \times 6 \times 64 \times 10^{-1}}{60} = 4$$

Since the unit cell contains 4 atoms, so it is face-centred cubic unit cell.

24. (b) : As the outer shell is dissolved in HCl, the outer layer of the egg will act as semipermeable membrane. Thus, on placing this in conc. NaCl solution exosmosis will happen. As a result egg will shrink.

25. (a, b, c) : (a), (b) and (c) show ferroelectricity whereas (d) shows antiferroelectricity.

26. (c) : In a closed packed lattice containing n particles,
number of tetrahedral voids = 2 × number of octahedral voids and
number of octahedral voids = number of atoms present in closed packed lattice
Hence, number of octahedral void = n
Number of tetrahedral void = $2n$.

27. (b) : In a close packing,
number of tetrahedral holes per atom = 2
Thus, ratio of atoms to tetrahedral holes = 1 : 2

28. (a) : O^{2-} ions occupy *hcp* arrangement,
Number of atoms per unit cell =

$$12 \times \frac{1}{6} + 3 + 2 \times \frac{1}{2} = 6$$

In *hcp* arrangement,
No. of octahedral voids =
no. of atoms present in *hcp* arrangement = 6.
Metal ions occupy 2/3rd of the octahedral void

$$= 6 \times \frac{2}{3} = 4$$

Hence formula of the compound will be M_4O_6 or M_2O_3. (simpler form)

29. (d) : A solution of two components is said to be ideal if each component of the solution obeys Raoult's law at all temperatures and concentrations. C_2H_5I + C_2H_5Br (at 40 °C), C_4H_9Cl + C_4H_9Br (at 50 °C) and *n*-hexane + *n*-heptane (at 30 °C) form ideal solution. Solution of C_2H_5OH + $CHCl_3$ shows positive deviation from Raoult's law, as A—B interactions are weaker than A—A and B—B interactions hence, this is a non-ideal solution.

30. (c) : The azeotrope solutions which show negative deviations from Raoult's law are called maximum boiling azeotropes because they have a composition having maximum boiling point and minimum vapour pressure.

31. (b) : As the solution becomes more and more dilute and approaches a limit of infinite dilution its components behave more ideally. The solvent obeys Raoult's law whereas the solute obeys Henry's law for an ideal dilute solution.

32. (b)

33. (c) : (P) Soda water = CO_2 in water (gas in liquid)
(Q) Sugar solution = sugar in water (solid in liquid)
(R) German silver = an alloy of Cu, Zn and Ni (solid in solid)
(S) Air = a mixture of gases (gas in gas)

34. (d)

35. (b) : Ferromagnetic property decreases from Fe to Ni because of decrease in the number of unpaired electrons.

36. (d) : Both being non-electrolytes with same molar concentration will have same decrease (not increment) in freezing point.
Both being in the form of their aqueous solutions, *i.e.*, solvent is same (water), K_f will be same for both.

37. (c) : Properties like referactive index, electrical conductance are identical in all directions for isotropic substances.

38. (c) : Raoult's law is not applicable for those electrolytes which produces a non-ideal solution.

39. (c) : In a lattice of N atoms, the number of tetrahedral sites is $2N$. We know that the conductivity of insulators is equal to 10^{-20} to $10^{-10}\ \Omega^{-1}\ m^{-1}$.

40. (a) : For isotonic solutions, $\pi_1 = \pi_2$
But $\pi = CRT$
Thus, at same temperature,
$\pi_1 = C_1RT$, $\pi_2 = C_2RT$,
if $\pi_1 = \pi_2$ then $C_1 = C_2$

41. (6) : In simple cubic cell, $a = 2r$, $Z = 1$

$$\text{Packing fraction} = \frac{\text{Occupied volume}}{\text{Total volume}}$$

$$= \frac{\left(\frac{4}{3}\right)\pi r^3}{a^3} = \frac{\left(\frac{4}{3}\right)\pi r^3}{(2r)^3} = \frac{\pi}{6}$$

Value of x is 6.

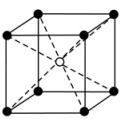
42. (9) : Molarity of orthophosphoric acid = 3 M

Now, basicity of orthophosphoric acid = 3

$\therefore$ Normality of orthophosphoric acid

$= 3\text{ M} \times 3 = 9\text{ N}$

43. (1) :



Unit cell of CsBr

Number of Br^- ions per unit cell

$$= 8 \text{ (at corners)} \times \frac{1}{8} = 1$$

Number of Cs^+ ion

$= 1$ (at the body centre) $\times 1 = 1$

44. (3) : 0.15 M urea, 0.15 M glucose have same concentration with 0.05 M $CaCl_2$.

0.05 M $CaCl_2$ gets dissolved in solution and gives three ions.

So, its concentration = $C \times i = 0.05 \times 3 = 0.15$ M

Concentration of $MgSO_4 = C \times i = 0.1 \times 2 = 0.2$ M

45. (3) : Molar volume $(a^3) = \frac{\text{Molar mass}}{\text{Density}} = \frac{58.5}{2.165}$

$$a = \left(\frac{58.5}{2.165}\right)^{1/3} = 3$$

46. (2) :

$$\frac{(\Delta T_b)_P}{(\Delta T_b)_Q} = \frac{K_b \times \left(\frac{w_B \times 1000}{M_B \times w_A}\right)_P}{K_b \times \left(\frac{w_B \times 1000}{M_B \times w_A}\right)_Q}$$

$$\frac{0.2}{0.4} = \frac{\left(\frac{0.1 \times 1000}{100 \times 100}\right)_P}{\left(\frac{0.1 \times 1000}{M_B \times 100}\right)_Q}$$

$$\frac{1}{2} = \frac{(M_B)_Q}{100}, \quad M_B = 50$$

$(M_B)_P : (M_B)_Q = 100 : 50 = 2 : 1$

Thus, $x = 2$.

47. (5) : Edge of the unit cell $(a) = 2 \times Y^{1/3}$ nm

Formula mass, $M = 6.023\ Y$ g mol^{-1}

$$= \frac{6.023Y}{1000} \text{ kg mol}^{-1}$$

For rock salt type structure, Z = 4

$$\therefore \quad \text{Density } (\rho) = \frac{Z \times M}{a^3 \times N_0}$$

$$= \frac{4 \times (6.023 \times 10^{-3} Y \text{ kg mol}^{-1})}{(2 \times Y^{1/3} \times 10^{-9}\text{ m})^3 \times (6.023 \times 10^{23}\text{ mol}^{-1})}$$

$= 5$ kg m^{-3}

48. (6) : Given: $P_A^\circ = 450$ mm, $P_B^\circ = 700$ mm,

$P_{total} = 600$ mm, $x_A = ?$

Applying Raoult's law, $P_A = x_A \times P_A^\circ$

$P_B = x_B \times P_B^\circ = (1 - x_A)P_B^\circ$

$P_{Total} = P_A + P_B = x_A \times P_A^\circ + (1 - x_A)P_B^\circ$

$= P_B^\circ + (P_A^\circ - P_B^\circ)x_A$

Substituting the given values, we get

$600 = 700 + (450 - 700)x_A$ or, $250\ x_A = 100$

or $x_A = \frac{100}{250} = 0.40$

Thus, composition of the liquid mixture will be

x_A (mole fraction of A) = 0.40

x_B (mole fraction of B) = 1 – 0.40 = 0.60

$\therefore \quad x = 6$

49. (6) : At low temperature, $AlCl_3$ exists as a close packed lattice of Cl^- ions with Al^{3+} ions occupying octahedral voids. Thus, Al^{3+} ions has 6 Cl^- ions around it. Hence, its coordination number is 6.

50. (5) : $\pi V = n\text{RT}$ or $\pi = \frac{n}{V} RT$

At 10 °C, $\frac{500}{760} = \frac{n}{V} \times R \times 283$ … (i)

Suppose the solution is diluted x times.

Then at 25 °C, $\frac{105.3}{760} = \frac{n}{xV} \times R \times 298$ … (ii)

Dividing eqn. (i) by eqn. (ii), we get

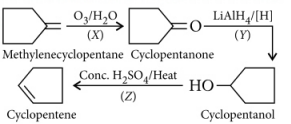
$$\frac{500}{760} \times \frac{760}{105.3} = x \times \frac{283}{298}$$

or $x = 5$, *i.e.*, the solution is diluted 5 times.

CHEMISTRY MUSING

SOLUTION SET 10

1. (c) :



Methylenecyclopentane, Cyclopentanone, Cyclopentene, Cyclopentanol

2. (c) : Oxidation : $Pb_{(s)} + SO_4^{2-}{}_{(aq)} \rightarrow PbSO_{4(s)} + 2e^-$

Reduction : $PbO_{2(s)} + 4H^+_{(aq)} + SO_4^{2-}{}_{(aq)} + 2e^- \rightarrow PbSO_{4(s)} + 2H_2O_{(l)}$

$$Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O_{(l)}$$

During discharging of battery H_2SO_4 is consumed. $W = ZIt$

Mass of H_2SO_4 = 2 moles = 2 × 98 g

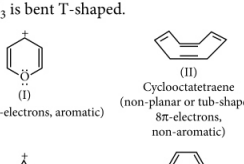
$$\therefore \quad Z = \frac{\text{Eq. wt. of } H_2SO_4}{96500}$$

$$\therefore \quad W = \frac{2\times98\times2.5\times965\times60}{2\times96500}$$

$$= 147 \text{ g} = \frac{147}{98} \text{ mol} = 1.50 \text{ mol}$$

3. (d) : BrF_3 is bent T-shaped.

4. (c) :



(I) (planar, 6p-electrons, aromatic)

(II) Cyclooctatetraene (non-planar or tub-shaped, 8π-electrons, non-aromatic)

(III) Cyclopropenyl cation (planar, 2π-electrons, aromatic)

(IV) Thiophene (planar, 6π-electrons completely delocalized over the entire ring, aromatic)

5. (d) : Hydration energies are calculated as

$BeF_2 = -2494 + 2 \times (-457) = -3408$ kJ mol^{-1}

$MgF_2 = -1921 + 2 \times (-457) = -2835$ kJ mol^{-1}

$CaF_2 = -1577 + 2 \times (-457) = -2491$ kJ mol^{-1}

$BaF_2 = -1305 + 2 \times (-457) = -2219$ kJ mol^{-1}

Lattice energies are given as

$BeF_2 = -2906$ kJ mol^{-1} ; $MgF_2 = -2610$ kJ mol^{-1}

$CaF_2 = -2459$ kJ mol^{-1} ; $BaF_2 = -2367$ kJ mol^{-1}

Then, $\Delta H_{solution}$ are

$BeF_2 = -3408 - (-2906) = -502$ kJ mol^{-1}

$MgF_2 = -2835 - (-2610) = -225$ kJ mol^{-1}

$CaF_2 = -2491 - (-2459) = -32$ kJ mol^{-1}

$BaF_2 = -2219 - (-2367) = +148$ kJ mol^{-1}

$\Delta H_{solution}$ is +ve in BaF_2, hence BaF_2 is easily soluble in water.

6. (b) : Moles of ZnS $= \dfrac{\text{Mass}}{\text{Molar mass}}$

$= \dfrac{68.3}{(65.72 + 32.07)}$ [∵ Mol. wt. of Zn = 65.72, S = 32.07]

= 0.698 mol

$$\Delta H = \frac{q_p}{\text{Moles of ZnS}} = \frac{-320}{0.698} = -458.45 \text{ kJ}$$

(For 1 mole of ZnS)

For 2 moles of ZnS, $\Delta H = -458.45 \times 2$

$= -916.9$ kJ/mol

7. (c) : Tetrahedral voids are found to be present on the body diagonals, two on each body diagonal at one-fourth of the distance from each end.

8. (a) : O^{2-} ions occupy *hcp* arrangement.

No. of atoms per unit cell $= 12 \times \frac{1}{6} + 3 + 2 \times \frac{1}{2} = 6$

In *hcp* arrangement,

No. of octahedral voids =

No. of atoms present in *hcp* arrangement = 6

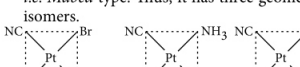
Metal ions occupy 2/3rd of the octahedral void

$$= 6 \times \frac{2}{3} = 4$$

Hence, formula is M_4O_6 or M_2O_3

9. (4) : Since Williamson synthesis occurs by S_N2 mechanism and primary alkyl halides are most reactive towards S_N2 reactions, therefore, best yields of unsymmetrical ethers are obtained when the alkyl halides are primary. However, the alkoxides may be either primary, secondary or tertiary. Thus, only four ethers *i.e.*, $C_6H_5CH_2OC_6H_5$, $(CH_3)_3COCH_2CH_3$, $C_6H_5OCH_2CH_3$ and $CH_3OCH_2CH_3$ can be prepared by Williamson synthesis.

10. (3) : $[Pt(CN)(Br)(PPh_3)(NH_3)]$ is a square planar complex with four different ligands *i.e. Mabcd* type. Thus, it has three geometrical isomers.



SOLVED PAPER 2014

WB-JEE

WEST BENGAL JOINT ENTRANCE EXAM

Arunava Sarkar, West Bengal

CATEGORY-I

Q. 1 to Q. 45 carry one mark each, for which only one option is correct. Any wrong answer will lead to deduction of 1/3 mark.

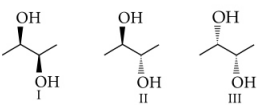
1. During the emission of a positron from a nucleus, the mass number of the daughter element remains the same but the atomic number
(a) is decreased by 1 unit
(b) is decreased by 2 units
(c) is increased by 1 unit
(d) remains unchanged.

2. Four gases *P*, *Q*, *R* and *S* have almost same values of '*b*' but their '*a*' values (*a*, *b* are van der Waals constants) are in the order $Q < R < S < P$. At a particular temperature, among the four gases the most easily liquefiable one is
(a) *P* (b) *Q*
(c) *R* (d) *S*

3. β-emission is always accompanied by
(a) formation of antineutrino and α-particle
(b) emission of α-particle and γ-ray
(c) formation of antineutrino and γ-ray
(d) formation of antineutrino and positron.

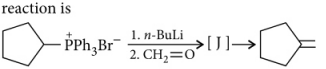
4. The values of ΔH and ΔS of a certain reaction are -400 kJ mol^{-1} and -20 kJ mol^{-1} K^{-1} respectively. The temperature below which the reaction is spontaneous is
(a) 100 K (b) 20 °C
(c) 20 K (d) 120 °C

5. The correct statement regarding the following compounds is



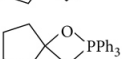
(a) all three compounds are chiral
(b) only I and II are chiral
(c) I and III are diastereomers
(d) only I and III are chiral.

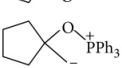
6. The intermediate 'J' in the following Wittig reaction is



(a) 

(b) 

(c) 

(d) 

7. Among the following compounds, the one(s) that gives (give) effervescence with aqueous $NaHCO_3$ solution is (are)

$(CH_3CO)_2O$	CH_3COOH
I	II
PhOH	CH_3COCHO
III	IV

(a) I and II (b) I and III
(c) only II (d) I and IV

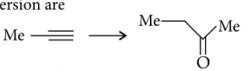
8. The system that contains the maximum number of atoms is
(a) 4.25 g of NH_3 (b) 8 g of O_2
(c) 2 g of H_2 (d) 4 g of He

9. Metal ion responsible for the Minamata disease is
(a) Co^{2+} (b) Hg^{2+}
(c) Cu^{2+} (d) Zn^{2+}

10. Among the following observations, the correct one that differentiates between SO_3^{2-} and SO_4^{2-} is
(a) both form precipitate with $BaCl_2$, SO_3^{2-} dissolves in HCl but SO_4^{2-} does not
(b) SO_3^{2-} forms precipitate with $BaCl_2$, SO_4^{2-} does not
(c) SO_4^{2-} forms precipitate with $BaCl_2$, SO_3^{2-} does not
(d) both form precipitate with $BaCl_2$, SO_4^{2-} dissolves in HCl but SO_3^{2-} does not.

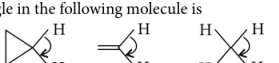
11. The pH of 10^{-4} M KOH solution will be
(a) 4 (b) 11
(c) 10.5 (d) 10

12. The reagents to carry out the following conversion are



(a) $HgSO_4$/dil. H_2SO_4
(b) BH_3; H_2O_2/NaOH
(c) OsO_4; HIO_4
(d) $NaNH_2/CH_3I$; $HgSO_4$/dil. H_2SO_4

13. The correct order of decreasing H — C — H angle in the following molecule is



(a) I > II > III (b) II > I > III
(c) III > II > I (d) I > III > II

14. $_{98}Cf^{246}$ was formed along with a neutron when an unknown radioactive substance was bombarded with $_6C^{12}$. The unknown substance was
(a) $_{91}Pa^{234}$ (b) $_{90}Th^{234}$
(c) $_{92}U^{235}$ (d) $_{92}U^{238}$

15. The rate of a certain reaction is given by, rate = $k[H^+]^n$. The rate increases 100 times when the pH changes from 3 to 1. The order (n) of the reaction is
(a) 2 (b) 0
(c) 1 (d) 1.5

16. ($_{32}Ge^{76}$, $_{34}Se^{76}$) and ($_{14}Si^{30}$, $_{16}S^{32}$) are examples of
(a) isotopes and isobars
(b) isobars and isotones
(c) isotones and isotopes
(d) isobars and isotopes.

17. The enthalpy of vaporization of a certain liquid at its boiling point of 35 °C is 24.64 kJ mol^{-1}. The value of change in entropy for the process is
(a) 704 J K^{-1} mol^{-1} (b) 80 J K^{-1} mol^{-1}
(c) 24.64 J K^{-1} mol^{-1} (d) 7.04 J K^{-1} mol^{-1}

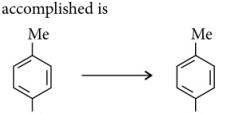
18. Given that
$C + O_2 \rightarrow CO_2$; $\Delta H^\circ = -x$ kJ
$2CO + O_2 \rightarrow 2CO_2$; $\Delta H^\circ = -y$ kJ
The heat of formation of carbon monoxide will be
(a) $\frac{y-2x}{2}$ (b) $y + 2x$
(c) $2x - y$ (d) $\frac{2x-y}{2}$

19. Commercial sample of H_2O_2 is labeled as 10 V. Its % strength is nearly
(a) 3 (b) 6
(c) 9 (d) 12

20. In DNA, the consecutive deoxynucleotides are connected via
(a) phosphodiester linkage
(b) phosphomonoester linkage
(c) phosphotriester linkage
(d) amide linkage.

21. The reaction of aniline with chloroform under alkaline conditions leads to the formation of
(a) phenyl cyanide (b) phenyl isonitrile
(c) phenyl cyanate (d) phenyl isocyanate.

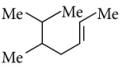
22. The reagent with which the following reaction is best accomplished is



(a) H_3PO_2 (b) H_3PO_3
(c) H_3PO_4 (d) $NaHSO_3$

23. At a certain temperature the time required for the complete diffusion of 200 mL of H_2 gas is 30 minutes. The time required for the complete diffusion of 50 mL of O_2 gas at the same temperature will be
(a) 60 minutes (b) 30 minutes
(c) 45 minutes (d) 15 minutes.

24. The IUPAC name of the following molecule is

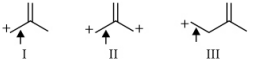


(a) 5, 6-dimethylhept-2-ene
(b) 2, 3-dimethylhept-5-ene
(c) 5, 6-dimethylhept-3-ene
(d) 5-isopropylhex-2-ene.

25. For one mole of an ideal gas the slope of V *vs.*T curve at constant pressure of 2 atm is X lit mol^{-1} K^{-1}. The value of the ideal universal gas constant 'R' in terms of X is
(a) X lit atm mol^{-1} K^{-1}
(b) $X/2$ lit atm mol^{-1} K^{-1}
(c) $2X$ lit atm mol^{-1} K^{-1}
(d) $2X$ atm lit^{-1} mol^{-1} K^{-1}

26. An atomic nucleus having low n/p ratio tries to find stability by
(a) the emission of an α-particle
(b) the emission of a positron
(c) capturing an orbital electron (K-electron capture)
(d) emission of a β-particle.

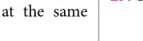
27. The correct order of decreasing length of the bond as indicated by the arrow in the following structures is



(a) I > II > III (b) II > I > III
(c) III > II > I (d) I > III > II

28. If Cl_2 is passed through hot aqueous NaOH, the products formed have Cl in different oxidation states. These are indicated as
(a) −1 and +1 (b) −1 and +5
(c) +1 and +5 (d) −1 and +3

29. In the following reaction, the product E is



(a)  (b) 
(c)  (d) 

30. The amount of electrolytes required to coagulate a given amount of AgI colloidal solution (−ve charge) will be in the order
(a) $NaNO_3 > Al(NO_3)_3 > Ba(NO_3)_2$
(b) $Al(NO_3)_3 > Ba(NO_3)_2 > NaNO_3$
(c) $Al(NO_3)_3 > NaNO_3 > Ba(NO_3)_2$
(d) $NaNO_3 > Ba(NO_3)_2 > Al(NO_3)_3$

31. The value of ΔH for cooling 2 mole of an ideal monoatomic gas from 225 °C to 125 °C at constant pressure will be [given $C_p = \frac{5}{2}R$]
(a) 250 R (b) −500 R
(c) 500 R (d) −250 R

32. The quantity of electricity needed to separately electrolyse 1 M solution of $ZnSO_4$, $AlCl_3$ and $AgNO_3$ completely is in the ratio of
(a) 2 : 3 : 1 (b) 2 : 1 : 1
(c) 2 : 1 : 3 (d) 2 : 2 : 1

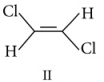
33. The emission spectrum of hydrogen discovered first and the region of the electromagnetic spectrum in which it belongs, respectively are
(a) Lyman, ultraviolet (b) Lyman, visible
(c) Balmer, ultraviolet (d) Balmer, visible.

34. As per de Broglie's formula a macroscopic particle of mass 100 g and moving at a velocity of 100 cm s^{-1} will have a wavelength of
(a) 6.6×10^{-29} cm (b) 6.6×10^{-30} cm
(c) 6.6×10^{-31} cm (d) 6.6×10^{-32} cm

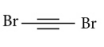
35. The electronic configuration of Cu is
(a) [Ne]$3s^2 3p^6 3d^9 4s^2$
(b) [Ne]$3s^2 3p^6 3d^{10} 4s^1$
(c) [Ne]$3s^2 3p^6 3d^3 4s^2 4p^6$
(d) [Ne]$3s^2 3p^6 3d^5 4s^2 4p^4$

36. The compound that will have a permanent dipole moment among the following is


I

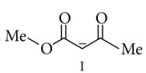

II

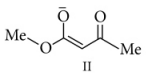

III

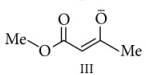

IV

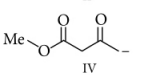
(a) I (b) II
(c) III (d) IV

37. Among the following structures the one which is not a resonating structure of others is


I

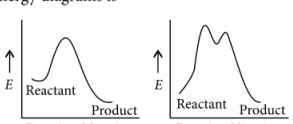

II


III


IV

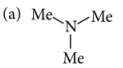
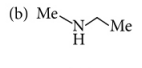
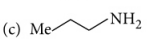
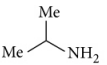
(a) I (b) II
(c) III (d) IV

38. The correct statement regarding the following energy diagrams is



(a) Reaction *M* is faster and less exothermic than reaction *N*
(b) Reaction *M* is slower and less exothermic than reaction *N*
(c) Reaction *M* is faster and more exothermic than reaction *N*
(d) Reaction *M* is slower and more exothermic than reaction *N*.

39. An amine C_3H_9N reacts with benzene sulphonyl chloride to form a white precipitate which is insoluble in aq. NaOH. The amine is

(a) 
(b) 
(c) 
(d) 

40. Among the followings, the one which is not a "greenhouse gas", is
(a) N_2O (b) CO_2
(c) CH_4 (d) O_2

41. The number of amino acids and number of peptide bonds in a linear tetrapeptide (made of different amino acids) are respectively
(a) 4 and 4 (b) 5 and 5
(c) 5 and 4 (d) 4 and 3

42. The 4th higher homologue of ethane is
(a) butane (b) pentane
(c) hexane (d) heptane.

43. The hydrides of the first elements in groups 15-17, namely NH_3, H_2O and HF respectively show abnormally high values for melting and boiling points. This is due to
(a) small size of N, O and F
(b) the ability to form extensive intermolecular H-bonding
(c) the ability to form extensive intramolecular H-bonding
(d) effective van der Waals interaction.

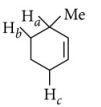
44. The two half cell reactions of an electrochemical cell is given as :
$Ag^+ + e^- \rightarrow Ag$; $E^\circ_{Ag^+/Ag} = -0.3995$ V
$Fe^{++} \rightarrow Fe^{+++} + e^-$; $E^\circ_{Fe^{+++}/Fe^{++}} = -0.7120$ V
The value of cell EMF will be
(a) – 0.3125 V (b) 0.3125 V
(c) 1.114 V (d) – 1.114 V

45. In case of heteronuclear diatomics of the type *AB*, where *A* is more electronegative than *B*, bonding molecular orbital resembles the character of *A* more than that of *B*. The statement
(a) is false
(b) is true
(c) cannot be evaluated since data is not sufficient
(d) is true only for certain systems.

CATEGORY-II

Q. 46 to Q. 55 carry two marks each, for which only one option is correct. Any wrong answer will lead to deduction of 2/3 mark.

46. The order of decreasing ease of abstraction of hydrogen atoms in the following molecule is



(a) $H_a > H_b > H_c$ (b) $H_a > H_c > H_b$
(c) $H_b > H_a > H_c$ (d) $H_c > H_b > H_a$

47. The bond angle in NF_3(102.3°) is smaller than NH_3 (107.2°). This is because of
(a) large size of F compared to H
(b) large size of N compared to F
(c) opposite polarity of N in the two molecules
(d) small size of H compared to N.

48. The compressibility factor (Z) of one mole of a van der Waals gas of negligible 'a' value is

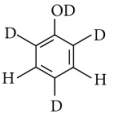
(a) 1 (b) $\frac{bP}{RT}$

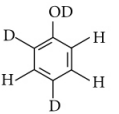
(c) $1+\frac{bP}{RT}$ (d) $1-\frac{bP}{RT}$

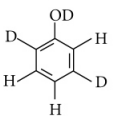
49. At 25 °C, the molar conductance of 0.007 M hydrofluoric acid is 150 mho cm^2 mol^{-1} and its Λ°_m = 500 mho cm^2 mol^{-1}. The value of the dissociation constant of the acid at the given concentration at 25 °C is
(a) 7×10^{-4} M (b) 7×10^{-5} M
(c) 9×10^{-3} M (d) 9×10^{-4} M

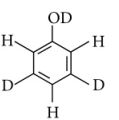
50. A piece of wood from an archaeological sample has 5.0 counts min^{-1} per gram of C-14, while a fresh sample of wood has a count of 15.0 min^{-1} $gram^{-1}$. If half-life of C-14 is 5770 years, the age of the archaeological sample is
(a) 8,500 years (b) 9,200 years
(c) 10,000 years (d) 11,000 years

51. When phenol is treated with D_2SO_4/D_2O, some of the hydrogens get exchanged. The final product in this exchange reaction is

(a) 

(b) 

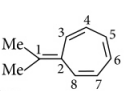
(c) 

(d) 

52. To observe an elevation of boiling point of 0.05 °C, the amount of a solute (Mol. wt. = 100) to be added to 100 g of water (K_b = 0.5) is
(a) 2 g (b) 0.5 g
(c) 1 g (d) 0.75 g

53. The structure of XeF_6 is experimentally determined to be distorted octahedron. Its structure according to VSEPR theory is
(a) octahedron
(b) trigonal bipyramid
(c) pentagonal bipyramid
(d) tetragonal bipyramid.

54. The most likely protonation site in the following molecule is



(a) C-1 (b) C-2
(c) C-3 (d) C-6

55. The volume of ethyl alcohol (density 1.15 g/cc) that has to be added to prepare 100 cc of 0.5 M ethyl alcohol solution in water is
(a) 1.15 cc (b) 2 cc
(c) 2.15 cc (d) 2.30 cc

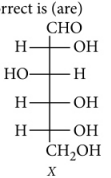
CATEGORY-III

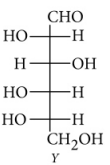
Q. 56 to Q. 60 carry two marks each, for which one or more than one options may be correct. Marking of correct options will lead to a maximum mark of two on pro rata basis. There will be no negative marking for these questions. However, any marking of wrong option will lead to award of zero mark against the respective question – irrespective of the number of correct options marked.

56. Cupric compounds are more stable than their cuprous counterparts in solid state. This is because

(a) the endothermic character of the 2nd *I. P.* of Cu is not so high
(b) size of Cu^{2+} is less than Cu^{+}
(c) Cu^{2+} has stabler electronic configuration as compared to Cu^{+}
(d) the lattice energy released for cupric compounds is much higher than Cu^{+}.

57. Among the following statements about the molecules *X* and *Y*, the one(s) which is (are) correct is (are)





(a) *X* and *Y* are diastereomers
(b) *X* and *Y* are enantiomers
(c) *X* and *Y* are both aldohexoses
(d) *X* is a *D*-sugar and *Y* is an *L*-sugar.

58. For a spontaneous process, the correct statement(s) is (are)
(a) $(\Delta G_{system})_{T,P} > 0$
(b) $(\Delta S_{system}) + (\Delta S_{surroundings}) > 0$
(c) $(\Delta G_{system})_{T,P} < 0$
(d) $(\Delta U_{system})_{T,V} > 0$

59. The formal potential of Fe^{3+}/Fe^{2+} in a sulphuric acid and phosphoric acid mixture (E° = +0.61 V) is much lower than the standard potential (E° = +0.77 V). This is due to
(a) formation of the species $[FeHPO_4]^+$
(b) lowering of potential upon complexation
(c) formation of the species $[FeSO_4]^+$
(d) high acidity of the medium.

60. Two gases *X* (Mol. wt. M_X) and *Y* (Mol. wt. M_Y; $M_Y > M_X$) are at the same temperature *T* in two different containers. Their root mean square velocities are C_X and C_Y respectively. If the average kinetic energies per molecule of two gases *X* and *Y* are E_X and E_Y respectively, then which of the following relation(s) is (are) true?
(a) $E_X > E_Y$ (b) $C_X > C_Y$
(c) $E_X = E_Y = \frac{3}{2}RT$ (d) $E_X = E_Y = \frac{3}{2}k_BT$

SOLUTIONS

1. (a) : ${}^{A}_{Z}X \longrightarrow {}^{A}_{Z-1}Y + {}^{0}_{+1}e^{-}$

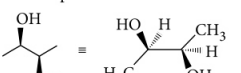
So, atomic number is decreased by 1 unit.

2. (a) : More the value of *a*, more will be the forces of attraction of between the gaseous molecules thus, more easily the gas will be liquefied.

3. (c): With the release of antineutrino and γ-ray, extra energy releases.

4. (c): $\Delta G = \Delta H - T\Delta S$
Now, for a reaction to be spontaneous, $\Delta G < 0$
$\therefore \quad \Delta H - T\Delta S < 0$
$\Rightarrow \quad -400 - T(-20) < 0 \quad \Rightarrow \quad -400 + 20\,T < 0$
$\therefore \quad 20\,T < 400 \quad \Rightarrow \quad T < 20$ K

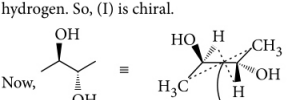
5. (d) : Look at the structures and orientation of groups in 3-D space :



(I)

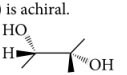
It has no plane of symmetry (look at the orientation of $-CH_3$ groups), no axis of symmetry (rotation through any axis does not generate the indistinguishable structure) or no point of symmetry (which is possible if one side —OH group is represented by ◄OH and another side by ┈OH. Same also for hydrogen. So, (I) is chiral.

Now,



(II)

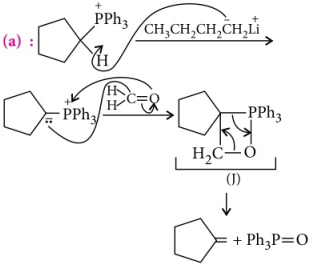
due to the presence of a centre of symmetry, structure (II) is achiral.



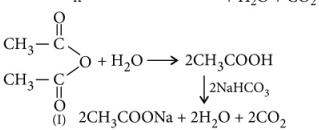
(III)

Again in this structure, there is no symmetry element. So, (III) is chiral.

6. (a) :



7. (a) : $CH_3COOH + NaHCO_3 \longrightarrow \underset{II}{CH_3COONa} + H_2O + CO_2$



8. (c): Gram molecular mass of NH_3 is 17 g.

$\therefore$ No. of molecules in 4.25 g of NH_3

$$= \frac{4.25}{17} N_A = \frac{N_A}{4}$$

Now, one molecule of NH_3 contains 4 atoms.

$\therefore$ $\frac{N_A}{4}$ molecules contain $\frac{N_A}{4} \times 4 = N_A$ atoms.

Again, 32 g of $O_2 = N_A$ molecules $= 2N_A$ atoms

$\therefore$ 8 g of $O_2 = \frac{N_A}{32} \times 8 = \frac{N_A}{4}$ molecules

$$= \frac{2N_A}{32} \times 8 = \frac{N_A}{2} \text{ atoms}$$

On the other hand,

2 g of $H_2 = N_A$ molecules $= 2N_A$ atoms

4 g of He $= N_A$ atoms

[$\because$ gram atomic mass of He = 4 g]

9. (b)

10. (a) : $BaCl_2$ forms white ppt. with both SO_3^{2-} and SO_4^{2-}.

$BaCl_2 + SO_3^{2-} \longrightarrow \underset{\text{white ppt.}}{BaSO_3\downarrow} + 2Cl^-$

$BaCl_2 + SO_4^{2-} \longrightarrow \underset{\text{white ppt.}}{BaSO_4\downarrow} + 2Cl^-$

However, only $BaSO_3$ dissolves in HCl through the following reaction :

$BaSO_3 + 2HCl \longrightarrow BaCl_2 + SO_2\uparrow + H_2O$

11. (d) : $KOH \longrightarrow K^+ + OH^-$

10^{-4} M $\qquad$ 10^{-4} M

$\therefore$ $[OH^-] = 10^{-4}$ M

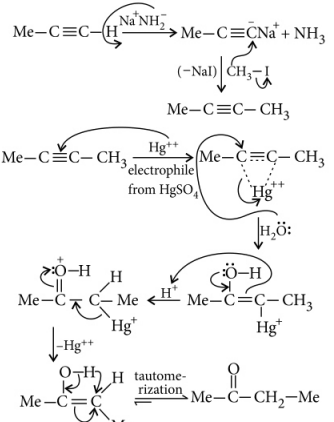
$\therefore$ $pOH = -\log_{10}[OH^-] = -\log_{10}(10^{-4}) = 4$

$\therefore$ $pH = 14 - 4 = 10$

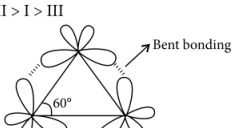
12. (d) : Me — C≡C(H) (Terminal alkyne)

sp-hybridised ; acidic hydrogen

$NaNH_2$ will abstract the acidic hydrogen. In fact, NH_2^- which is a strong base will abstract the acidic hydrogen.



13. (b) : II > I > III



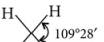
Look at the structure carefully. In cyclopropane, C—C bonds are bent and not pure σ-bonds. Overlapping is greatest when orbitals overlap

"end-on" *i.e. via* σ-bonding. π-bonds overlap laterally. The overlap in cyclopropane is neither end-on nor lateral but in between. So, it is intermediate between σ- and π-bonding.

So,  This is > 109°28′ but < 120°

(I)

(II)



(III)

Thus, the correct order of decreasing H — C — H angle is : II > I > III

14. (c): Let the unknown substance is ${}^{A}_{Z}Q$

$${}^{A}_{Z}Q + {}^{12}_{6}C \longrightarrow {}^{246}_{98}Cf + {}^{1}_{0}n$$

$\therefore \quad Z + 6 = 98 \quad \Rightarrow \quad Z = 92$

$A + 12 = 246 + 1 \Rightarrow A = 235$

So, the unknown substance is ${}^{235}_{92}U$.

15. (c): Rate $(r) = k[H^+]^n$

When pH = 3 ; $[H^+] = 10^{-3}$

and when pH = 1 ; $[H^+] = 10^{-1}$

$$\therefore \quad \frac{r_1}{r_2} = \frac{k(10^{-3})^n}{k(10^{-1})^n} \Rightarrow \frac{1}{100} = \left(\frac{10^{-3}}{10^{-1}}\right)^n$$

$(\because r_2 = 100\, r_1)$

$\Rightarrow (10^{-2})^1 = (10^{-2})^n \Rightarrow n = 1$

16. (b) :

${}^{76}_{32}Ge \rightarrow$ protons = 32 = electrons, neutrons = 76 − 32 = 44

${}^{76}_{34}Se \rightarrow$ protons = 34 = electrons, neutrons = 76 − 34 = 42

Mass no. same but atomic no. different. So, they are isobars.

${}^{30}_{14}Si \rightarrow$ protons = 14 = electrons, neutrons = 30 − 14 = 16

${}^{32}_{16}S \rightarrow$ protons = 16 = electrons, neutrons = 32 − 16 = 16

Same no. of neutrons. So, they are isotones.

17. (b) : We know, $\Delta S_{vap} = \dfrac{\Delta H_{vap}}{T_b}$

$$\Rightarrow \quad \Delta S_{vap} = \frac{24.64 \times 10^3}{(35+273)} \text{ J mol}^{-1} \text{ K}^{-1}$$

$$= 80 \text{ J K}^{-1} \text{ mol}^{-1}$$

18. (a) : (1) $C + O_2 \longrightarrow CO_2$; $\Delta H_1^\circ = -x$ kJ

(2) $2CO + O_2 \longrightarrow 2CO_2$; $\Delta H_2^\circ = -y$ kJ

Desired equation for formation of CO is

$$C + \frac{1}{2}O_2 \longrightarrow CO$$

This equation can be obtained by

$[(1) + \frac{1}{2}$ (reverse of (2))] *i.e.*

$$C + O_2 + CO_2 \longrightarrow CO_2 + CO + \frac{1}{2}O_2$$

$$\therefore \quad \Delta H_f^\circ(CO) = -x + \frac{1}{2}(+y) = \frac{y}{2} - x = \frac{y - 2x}{2}$$

19. (a) : 10 V (10 volume) H_2O_2 means that 1 mL of H_2O_2 solution will produce 10 mL of O_2 at STP.

Now, decomposition of H_2O_2 is as below :

$2H_2O_2 \longrightarrow 2H_2O + O_2$

(2 × 34) g = 68 g ; 22400 mL (at STP)

$\therefore$ 22400 mL of O_2 is obtained from 68 g of H_2O_2

$\therefore$ 10 mL of O_2 is obtained from $\dfrac{68}{22400} \times 10$ g of H_2O_2

$= 0.03036$ g of H_2O_2

but this 10 mL of O_2 corresponds to 0.03 g of H_2O_2 solution approximately.

Therefore, 1 mL of H_2O_2 solution contains 0.03 g of H_2O_2

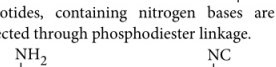
$\therefore$ 100 mL of H_2O_2 solution contains 3 g of H_2O_2

$\therefore$ % strength is 3.

20. (a): Phosphodiester linkage is .

Nucleotides, containing nitrogen bases are connected through phosphodiester linkage.

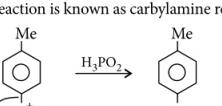
21. (b) :



Aniline — Phenyl isonitrile

This reaction is known as carbylamine reaction.

22. (a) :



H_3PO_2 is monobasic acid.

23. (b) : According to Graham's law of diffusion or effusion.

Rate of diffusion of a gas (r)

$$= \frac{\text{Volume of the gas diffused } (V)}{\text{Time taken for the diffusion } (t)}$$

Now, according to Graham's law,

$$r \propto \frac{1}{\sqrt{\text{Molecular mass of the gas}}}$$

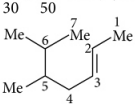
i.e. $r \propto \frac{1}{\sqrt{M}}$

Now, $\frac{r_{H_2}}{r_{O_2}} = \sqrt{\frac{M_{O_2}}{M_{H_2}}} \Rightarrow \frac{200/30}{50/t} = \sqrt{\frac{32}{2}}$

where, t is the time taken for diffusion of 50 mL of O_2 gas.

$$\Rightarrow \frac{200}{30} \times \frac{t}{50} = 4 \Rightarrow t = 30 \text{ min}$$

24. (a) :



5,6-Dimethylhept-2-ene

25. (c): We can take T to be the independent variable and V to be the dependent variable. Now, for one mole of an ideal gas,

$PV = RT$

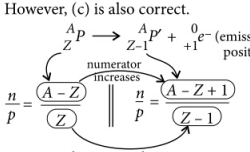
$$\Rightarrow \frac{V}{T} = \frac{R}{P} \Rightarrow \text{Slope} = \frac{R}{P} = X \text{ lit. mol}^{-1} \text{ K}^{-1}$$

$$\Rightarrow R = P \times X \text{ lit. mol}^{-1} \text{ K}^{-1}$$

$R = 2$ atm $\times X$ lit. mol^{-1} K^{-1} ($\because$ $P = 2$ atm)

$$\Rightarrow R = 2X \text{ lit. atm mol}^{-1} \text{ K}^{-1}$$

26. (b) : More appropriate correct option is (b). However, (c) is also correct.



Again,

$$^{A}_{Z}P + {}^{0}_{-1}e \longrightarrow {}^{A}_{Z-1}P''$$

(from K-orbit of another element)

Here, also the same ratio can be shown.

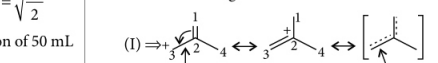
[P' and P'' may be same or different depending on the energy criteria. In most of the cases, they are same].

27. (c): In general,

C = C bond length is 1.33 Å

C – C bond length is 1.54 Å

(I) $\Rightarrow$

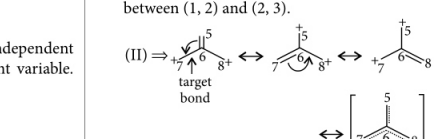


target bond

Partial double bond character at the target bond in the resonance hybrid structure. (charge has not been shown.)

In structure (I) resonance is concentrated between (1, 2) and (2, 3).

(II) $\Rightarrow$

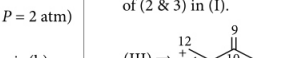


target bond

Resonance hybrid (charge has not been shown.)

Here, resonance is concentrated in between (5, 6), (6, 7) and (6, 8). So, partial double bond character is lesser in between (6 & 7) than that of (2 & 3) in (I).

(III) $\Rightarrow$



target bond

pure single bond; no resonance

So, the order of single bond character is :

11 – 12 > 6 – 7 > 2 – 3

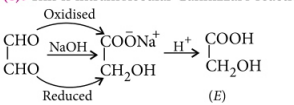
Thus, bond length order will be III > II > I.

28. (b) : With hot and concentrated aqueous NaOH (though 'concentrated' was not mentioned in

the question paper, however, it should have been), Cl_2 reacts as below :

$$\overset{0}{3Cl_2} + 6NaOH \longrightarrow \underset{\text{(sodium chloride)}}{5\overset{-1}{NaCl}} + \underset{\text{(sodium chlorate)}}{\overset{+5}{NaClO_3}} + 3H_2O$$
(hot, conc.)

29. (c): This is intramolecular Cannizzaro reaction.



30. (d) : According to Hardy Schulze law, for coagulation,

$$\text{Quantity of electrolyte} \propto \frac{1}{\text{Charge on the cation/anion}}$$

To coagulate AgI, I^- (–ve charge) is to be coagulated.

$Al(NO_3)_3 \longrightarrow 2Al^{3+} + 3NO_3^-$

$Ba(NO_3)_2 \longrightarrow Ba^{2+} + 2NO_3^-$

$NaNO_3 \longrightarrow Na^+ + NO_3^-$

Charge on the cation decreases in the order : $Al^{3+} > Ba^{2+} > Na^+$

Thus, the amount of electrolytes required will be in the order : $NaNO_3 > Ba(NO_3)_2 > Al(NO_3)_3$

31. (b) : $\Delta H = nC_p\Delta T$ ($n = 2$, $C_p = 5\ R/2$)

$\Delta T = (125 - 225)°C = -100\ °C = -100\ K$

$$\Rightarrow \quad \Delta H = 2 \times \frac{5R}{2}(-100) = -500\ R$$

32. (a) : Zn^{2+} (1 M) + $2e^-$ ⟶ Zn ; 2 Faraday

Al^{3+} (1 M) + $3e^-$ ⟶ Al ; 3 Faraday

Ag^+ (1 M) + e^- ⟶ Ag ; 1 Faraday

Ratio of quantity of electricity required = 2 : 3 : 1.

33. (d) : Balmer series was discovered during the year 1885 whereas Lyman series was discovered in 1906. Balmer series lies in the visible region whereas Lyman series in the UV zone.

34. (c): Mass (m) = 100 g; velocity (v) =100 cm s^{-1}

According to de Broglie's equation,

$$\lambda = \frac{h}{mv}$$

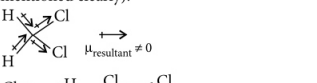
$$\lambda = \frac{6.626 \times 10^{-27}}{100 \times 100} = 6.6 \times 10^{-31}\ \text{cm}$$

35. (b) : Cu(29) : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$ (using Aufbau principle and Hund's rule of maximum multiplicity.)

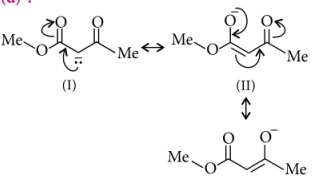
Ne(10) : $1s^2 2s^2 2p^6$

So, Cu(29) : [Ne] $3s^2 3p^6 3d^{10} 4s^1$

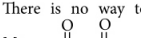
36. (a) : Permanent dipole moment means a fixed value of dipole moment (this should have been mentioned clearly).



37. (d) :

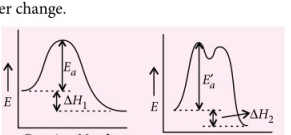


There is no way to get structure (IV) *i.e.*



because it has violated the basic rule for resonance. Here, one hydrogen has been removed; this is never possible as in resonance, no. of atoms and position of atoms never change.

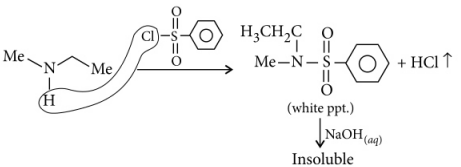
38. (c):



$E_a < E'_a$. So, reaction M is faster.

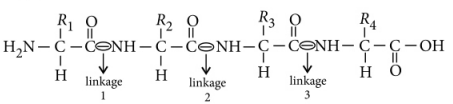
$\Delta H_1 > \Delta H_2$; so, reaction M is more exothermic.

39. (b) : 2° amine reacts with benzene sulphonyl chloride and the product formed is insoluble in NaOH. Therefore, the amine should have only one H-atom attached to nitrogen atom.



40. (d) : O_2 is not a gas responsible for the rise in temperature of the earth.

41. (d) : In general,
No. of peptide bonds = No. of amino acids – 1



42. (c): $C_2H_6 + (CH_2)_4 \longrightarrow \underset{\text{(Hexane)}}{C_6H_{14}}$

In homologous series any two successive compounds have a difference of $-CH_2$ group. Here, it is asked for the 4th higher homologue.

43. (b) :

Atom	Electronegativity in Pauling scale
F	4.0
O	3.5
N	3.0

Thus, NH_3, H_2O and HF can form extensive intermolecular H-bonding.

44. (b) : As per the reduction potential values, Ag will act as cathode and Fe will act as anode.
Cell reactions will be

At cathode : $Ag^+ + e^- \longrightarrow Ag$

At anode : $Fe^{2+} \longrightarrow Fe^{3+} + e^-$

$$Ag^+ + Fe^{2+} \longrightarrow Ag + Fe^{3+}$$

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode})$$

(Redn. pot. value)

So, $E^\circ_{cell} = E^\circ_{Ag^+/Ag} - E^\circ_{Fe^{3+}/Fe^{2+}}$

$= [-0.3995 - (-0.7120)]\ V = 0.3125\ V$

45. (b) : BMOs resemble with the more electronegative atom. More electronegative atoms are lower in energy and this is due to the hold on the electrons by the nucleus.

46. (b) **47. (c)** **48. (c)** **49. (d)**
50. (b) **51. (a)** **52. (c)** **53. (c)**
54. (a) **55. (b)** **56. (b, d)** **57. (b, c, d)**
58. (b, c) **59. (a, b)** **60. (b, d)**

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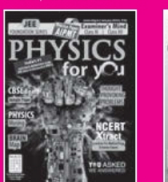

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